FACTORS UNDERLYING THE COMBUSTION OF CARBON AT HIGH TEMPERATURES

THESIS

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CHAPTER 1

THE NATURE OF GRAPHITE AND AMORPHOUS CARBON

Before considering the combustion of carbon it is desirable to know something of the molecular nature of the material with which we are dealing. It is usual to classify the various forms of carbon as having either a diamond, graphite or an amorphous type of structure and it is with the two latter forms that we shall deal here.

The structure of graphite has been established by X-ray and chemical methods and it is shown to consist of flat hexagon planes with a carbon-carbon bond distance of 1.42 Å., the distance between the planes being 3.35 Å. (Fig. 1). Roth suggested, from data on heat of combustion, that there were at least two different forms of graphite, termed "α" and "β", but this was not substantiated by the more accurate determinations of later workers[1]. Since then, Lipson and Stokes[2] have shown that X-ray diffraction films indicate the existence of a modification of graphite in which the hexagonal layers are arranged with the fourth vertically over the first (the third layer is vertically over the first in the more usual structure) and this new form may be present to the extent of about 10 per cent. in natural graphite. Ruff has suggested that the differences in energy content and density between different samples of graphite may be due to the presence of faults in the graphite lattice.

Although there are powerful forces between the atoms of the layer planes of graphite, the inter-planar bond is extremely weak; it is estimated by Ruff[3] to be about one sixth of the strength of the bond between neighbouring carbon atoms in the same plane, whilst Pauling,

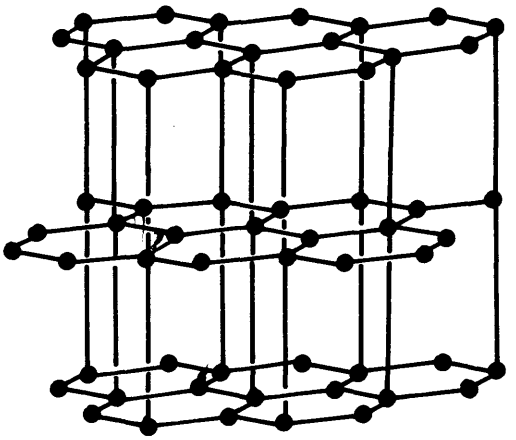

Fig. 1.- The structure of graphite.

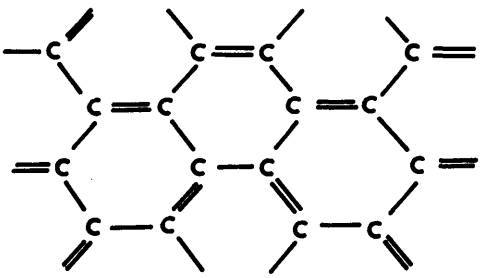

Fig. 2.- One third double bond character of carbon atom in the graphite lattice.

Brockway and Beach[4] tend to neglect it altogether when they assume that each bond has a one third double bond character corresponding to resonance among such structures as Fig. 2. The high thermal and electrical conductivity of graphite, comparable to that of many metals, suggests that the inter-planar bond may be regarded as a weak one dimensional metallic valency, and chemical evidence leads us to regard the graphite layer-planes as large free radicles bonded by weak valency forces to form graphite crystallites. Riley[5] has summarized in detail the similarity of the chemistry of graphite to that of the triarylmethyls. It is evident from Fig. 3 that if we consider one particular carbon atom in the graphite lattice then its three valency bonds lead to three aromatic hexagons and its properties might be expected to be similiar to those of the central carbon atom of the triphenylmethyl group. The evidence accumulated leaves little doubt as to the pronounced aromatic character of the hexagon layer-planes in pure graphite.

Our views on the structure of the so-called amorphous carbons have been considerably modified over the last few years. As early as 1874 Weber[6] stated that the specific heats gave no evidence of three intrinsically different forms of carbon and this was confirmed by Debye and Scherrer[7] who showed that the X-ray spectra of both graphite and amorphous carbon indicated the same internal crystal structure. There is abundant chemical evidence to support these views. Both graphite and amorphous carbon, e.g., soot, can form layered lattice structures such as C_8K, $C_{16}K$, $(CF)_n$, etc., whilst Juetter[8] has shown that the yields of mellitic acid, $C_6(CO_2H)_6$, a derivative of benzene, obtained from carbonaceous materials heated to 1000 C. are of the same order

as those obtained from graphite. The fact that the specific gravity of the solid products of carbonisation is of the order of 1.9 as compared with the value of 2.25 for pure graphite is explained by the fact that, like most forms of commercial carbon, small quantities of gas (hydrogen, carbon monoxide) are present between the graphite planes, thus preventing their coalescence and subsequent increase in density[9, 10].

Blayden, Gibson and Riley[11] have carried out extensive work on coals , cokes and chars by means of the X-ray powder diffraction technique applied to series of closely related specimens. They suggest that coals and cokes[12] consist of platelets arranged in considerable disorder. Each platelet consists of several hexagon layer planes, whose edge atoms are linked to the non-carbon atoms present, and it is this which limits the growth of the platelet. By measuring the breadth of the diffraction lines on the X-ray powder photograph it is possible to obtain a figure which is called the average crystallite dimension and it is found that, in general, these carbon crystallites contain three or four layer planes. The latter, although parallel in any one crystallite are arranged in randomly orientated groups and this type of structure has been termed by Warren[13] "turbostratic". The ease with which the flat lamellae can move over one another appears to be decided by the presence of cross linkages (possibly through the agency of oxygen) and the terms rigid and mobile turbostratic systems have been coined. More recently[14] tilting of the aromatic hexagon planes similiar to that discussed by Karle and Brockway[15] for the structure of o-tetraphenylene and analogous to that for glass[16] has been put forward as a possible factor in the building

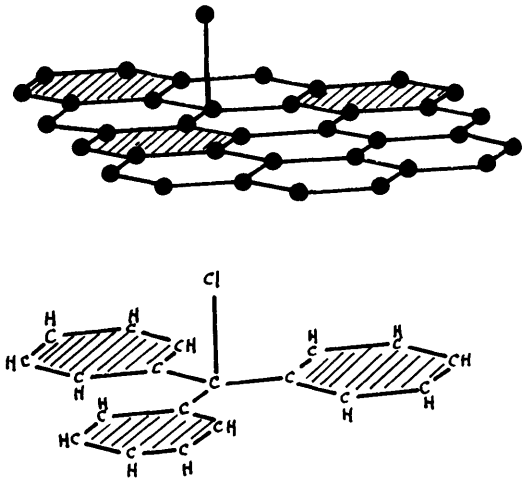

Fig. 3.- Similarity between a carbon atom in a graphite plane and in triphenylmethyl chloride.

up of cokes and chars.

As far as coal and coke are concerned we may agree with Bone[17] and say that there is a gradual transition of benzenoid properties as the degree of coalification or carbonization proceeds. The nature of the original substance and the presence of foreign atoms are both of paramount importance, and the higher the temperature of carbonization the more likely is the material to approximate to an ordered graphite lattice.

Apart from considerations of internal molecular structure, combustion is also related to the macro structure of the burning particle. It will be shown later that the rate of combustion of a particle is directly proportional to its superficial surface area. The ratio of true to superficial surface is difficult to determine in the case of a porous char or coke but it appears from preliminary calculations, that for a material of a given porosity, it will be little affected by pore size and distribution. Work is at present being carried out on the relationship of the two latter factors to combustibility in the case of blast furnace coke.*

* Work at present in progress at the Royal Technical College, Glasgow.

CHAPTER 11

THE MECHANISM OF CARBON COMBUSTION

Much work has been carried out on the carbon plus oxygen reaction both from a fundamental and an empirical point of view. In order to study the true surface reaction and avoid secondary reactions in the gas phase, it is necessary to conduct experiments at very low pressures, high gas velocities and with smooth carbon surfaces. Work of this kind has been carried out by Langmuir[18], Sihvonen[19] and Meyer[20], using electrically heated graphite filaments. In some cases and attempt has been made to correlate the results with the known structure of the graphite lattice (Sihvonen[19], Ruff[3]). More recently, Strickland Constable[21] has carried out low pressure experiments in a stationary atmosphere, and he suggests convincingly that the conflicting results of earlier workers in this field may have been due to the activation of gas molecules by thermionic emission from the electrically heated filaments. The results of this low pressure work cannot be extrapolated to provide information on the combustion mechanism at higher pressures because of the complex diffusion problems and the presence of secondary gas phase reactions in the latter case. Moreover, in the case of the mechanism in beds of carbon particles, there is the additional complication of reactions within the voids of the bed.[22, 23]

Rhead and Wheeler[24] must be given the credit for the first thorough investigation of the primary reaction between carbon and oxygen. They put forward the conception of a surface complex C_xO_y which then decomposed to give CO and CO_2. Similiar theories have since been put forward by Lowry and Hulett[25], Rideal and Wright[26], Shah[27], and several other workers. However , it has been pointed out

by Strickland-Constable[28] that the formation of a complex such as that suggested by Rhead and Wheeler would lead to a zero order reaction since the rate of formation of the complex is high and its rate of decomposition is low, whereas Lambert[29], Meyer[20], and Strickland-Constable[21] find the low temperature reaction (below 1500° Å.) to be of the first order. In addition, if surface compounds are formed as above, the rate of reaction of freshly outgassed charcoal should increase as oxidation proceeds because initially oxygen will be used up to form a layer of surface oxide and only at a later stage will this decompose to give carbon monoxide and carbon dioxide. The contrary is found to be the case for the analogous reaction of charcoal with nitrous oxide[30]. Strickland-Constable puts forward the hypothesis of two types of surface compound. One of these, an "intermediate" compound, is capable of oxidising carbon monoxide to carbon dioxide. He suggests that surface oxides are probably covalent compounds having a wide range of structure and thermal stability. This is borne out by Lowry and Hulett[25] who found that temperatures of at least 1000° C. were requiredto decompose all the solid oxides on charcoal. That these oxides may also, in certain cases, possess distinct acid and basic properties has been shown by Schilow, Schatanowskaja and Tschmutov[31]. Strickland-Constable assumes provisionally that the intermediate compounds are the least stable of the surface oxides (or merely adsorbed oxygen) and that they react with more oxygen or carbon monoxide in the gas phase to form carbon dioxide by means of a first order reaction.

Work on active forms of carbon indicates that oxygen may be able to penetrate the hexagon layer planes of a graphite structure

to form inter-planar oxides[32]. However, it should be remembered that the characteristic property of active carbon is its high specific surface reactivity which is due in part to an exceptionally large surface area and inter-planar oxide formation may be of less importance for a non-reactive carbon.

When considering the mechanism of the oxidation reaction at higher pressures the number of intermolecular collisions in the gas phase becomes of supreme importance. Several attempts have been made to calculate absolute reaction rates of combustion on the assumption that the rate of diffusion of oxygen molecules towards the burning surface must balance the rate of diffusion of combustion products away from the surface. Such methods are hampered by lack of detailed knowledge concerning the physical conditions existing in the combustion zone. Parker and Hottel[33] studied the gas film structure by microsampling of the adhering film and they calculated the diffusivities of carbon dioxide through nitrogen and oxygen through nitrogen. Some workers assume a film of stagnant gas to surround the burning specimen when the problem of gaseous diffusion in considerably simplified. Burke and Schumann[34] have applied this technique to the combustion of small particles (less than 0.5 mm. diameter) of pulverized fuel. Smith and Gudmundsen[35] describe experiments with carbon spheres of 4.6 mm. diameter, these being burnt in a stream of preheated air, and Mayers[36] has set up an empirical equation based on their results to correlate the rate of combustion with variations in temperature, pressure, gas velocity and particle radius. Tu, Davis, and Hottel[37] studied the rate of combustion of carbon spheres of 25 mm. diameter in dry preheated oxygen-nitrogen mixtures. The sphere was suspended in

such a way that it was able to rotate at a standardized rate of 20 r.p.m. As in the work of Smith and Gudmundsen the temperature of the burning specimen was measured by means of an optical pyrometer. Tu, Davis and Hottel divided the process of combustion into two zones - below about 1000° C. (surface temperature of the carbon), the rate of chemical reaction was said to control the rate of combustion and temperature was all important whereas above 1000° C. diffusion was suggested as the controlling factor and gas velocity became of greater importance. Using the Reynolds analogy of fluid flow these workers were able to calculate approximately the absolute magnitude of the rate of combustion although they state that this analogy tends to predict unduly thin gas films when applied to such problems. It may be noted here that the use of Rice's formula[38] by Burke and Schumann for the calculation of the stagnant gas film thickness has been queried by Mayers[36] on the grounds of work by Kennard[39] and by Fage and Townend[40] neither of whom obtained evidence of stationary films during their work on gas and liquid flow problems. However, since Kennard was dealing with the problem of temperature distribution surrounding bodies at temperatures of less than 150° C., and Fage and Townend were working on the flow of water in tubes at room temperatures, it seems unwise to apply the conclusions of these comparatively low temperature experiments to the high temperature combustion process. Nevertheless the existence of a stagnant film seems unlikely when one views the reaction on a coke surface by means of a high temperature microscope, the products of combustion being seen to disturb the fused ash at high temperatures. On the other hand the existence of such a film has proved fruitful for purposes of calculation and indeed the remarkable adherence of solid ash to burning coke (p. 19[1]) seems to justify such

an assumption in some cases.

Mayers[41] in some experiments on the rate of reduction of carbon dioxide by graphite, passed carbon dioxide over cylindrical specimens of electrode graphite and by increasing the gas flow rate until no further increase in the rate of reaction was observed he was able to assume that at this flow rate the partial pressure of carbon dioxide at the surface of the specimen was equal to the total pressure of gas, i.e., the velocity coefficient of partial pressure of carbon dioxide was zero. In his subsequent calculations only those values of zero velocity coefficient were used. This method might be used for the combustion of carbon in oxygen but it would entail very high reaction rates which would be difficult to follow experimentally.

Finniston[42] in a study of the combustion of coke used cylindrical specimens and burnt them in a stream of air at temperatures up to about 1500° C. He was able to show that the rate of combustion was directly proportional to the superficial surface area of the specimen and also to establish the validity of the Arrhenius conception of activation energy as applied to the combustion of coke. Reference will be made to this work later as it formed the starting point of the present research.

In conclusion, numerous empirical combustion tests have been designed for carbonaceous fuel beds, particularly coke, and it appears that physical conditions of sizing and voidage, etc., are of more importance than the specific reaction rate of the fuel substance. This subject has been discussed in some detail by Mayers[43] and by Hiles and Mott[44], the latter giving a summary of the Russian work in this field.

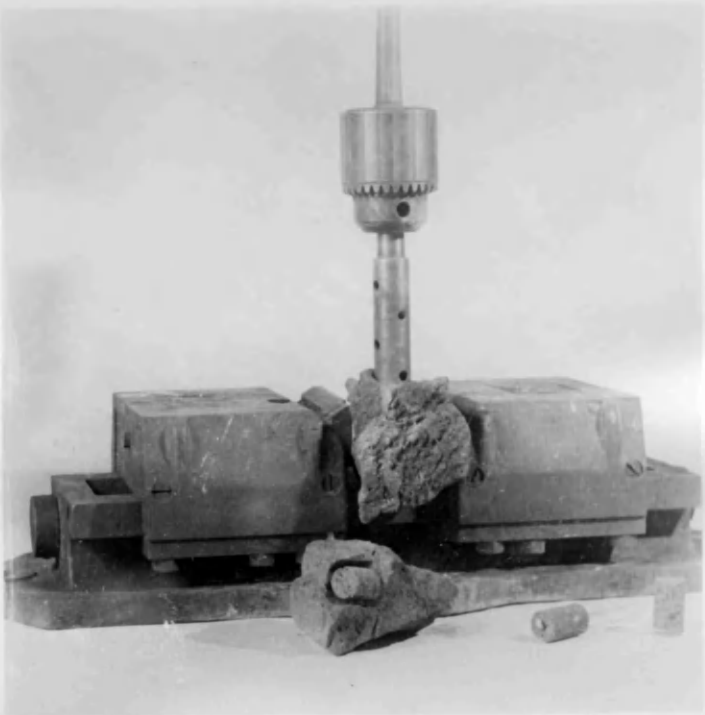

Plate 1.- Method of trepanning cylindrical coke specimens.

CHAPTER 111

THE COMBUSTIBILITY APPARATUS

As mentioned in the previous chapter it was decided to conduct further experiments along the lines of those carried out by H.M. Finniston[42] but with some means of varying the factors of gas velocity and pressure. It was felt, moreover, that the effect of the geometrical configuration of the combustion chamber in relation to the rate of combustion should be studied in some detail, as such variables as gas velocity and chamber diameter are mutually inter-dependent. The information from such geometrical considerations might also be of value when studying the effect of voidage and packing density in a fuel bed.

Although this work applies to the combustion of carbon in general, its application to the combustion of coke in the blast furnace for the production of pig iron has been kept constantly in view. For this reason most of the work has been carried out on specimens of coke, these being either cut from large pieces with a diamond cutting wheel and ground to shape or drilled out by means of a diamond tipped trepanning tool as shown in Plate 1. In the former case each specimen in the form of a cylinder measured 3.18 cm. long and 1.91 cm. diameter, whereas in the latter case the diameter was 1.83 cm. The trepanning method is much to be preferred both from the point of view of accuracy of shape and also labour involved, but the method is not suitable for badly fissured coke. The essential requirement is a high speed drill of extreme rigidity with provision for the application of ample water to the grinding surfaces. All specimens were finally drilled axially

with a $\frac{1}{8}$ in. (0.32 cm.) high speed steel drill for the purpose of suspension. As far as possible the coke specimens were free from cracks and they were cut from the centre of half-oven width pieces, i.e., the soft centre-oven ends and the badly fissured cauliflower ends were neglected. By this means it was possible to obtain specimens of approximately constant density from the same sample of coke, the weight remaining constant to within ±0.3 gm., the total weight of the specimen varying from 7 to 9 gm. according to the coke used.

Each specimen was suspended from a silica tube to which was fused a small platinum hook and this was then attached to a nichrome wire. The loss in weight of the suspension during a run, from reduction of the silica, was less than 0.01 gm. and could be neglected. At temperatures above 1550° C. the silica suspension was found to have insufficient strength to support the specimen and it was replaced by a fused alumina tube.

The gas for the combustion was drawn through the apparatus by means of vacuum pumps A and B (Fig. 4), the former being an Edwards Speedivac 1A with a rated capacity of 48 litres per minute, and the latter and Edwards Hyvac of 10 litres per minute capacity, this being used mainly as a standby when an extra large capacity was required and also for the purpose of calibrating the gas flow as described below. It was feared at first that the products of combustion containing sulphur dioxide (obtained from the oxidation of sulphur in the coke) might corrode the working parts of the pumps, but they functioned perfectly satisfactorily and no material damage appears to have been sustained over a period of some two and a half years, the vacuum oil being renewed about every six months.

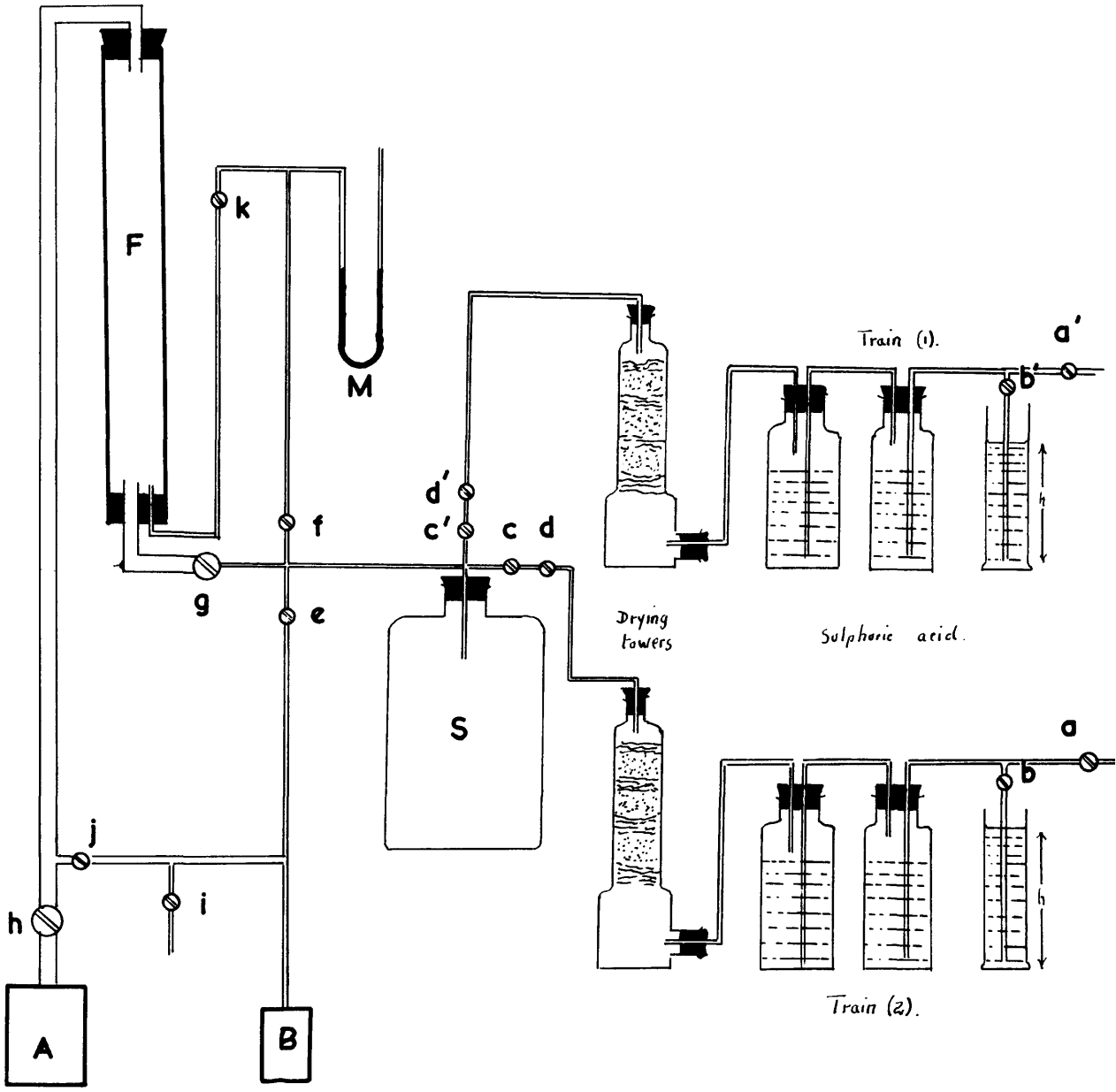

Fig. 4.- Gas flow diagram for the combustion apparatus.

When using air for combustion it was dried by drawing it through concentrated sulphuric acid and then through a tower packed with alternate layers of magnesium perchlorate and glass wool in Train (1) of Fig. 4. In order to study the effect of varying oxygen concentration, a second train (2) was added, and this could be supplied with either pure oxygen or pure nitrogen from cylinders of the compressed gas. Taps d and d' were used to regulate the flow of gas required and once these had been correctly adjusted for a particular rate of gas flow c and c' were used for "on" and "off" regulation only. Taps b and b' were left open and the gas cylinder valves adjusted to provide a slight excess of gas over that actually required, the excess being blown off to atmosphere, and in this way a constant pressure head h was maintained. From the drying towers the gases were passed to an 8 litre bottle S, thence through tap g to the combustion chamber F. Owing to the fact that in some cases gas was being supplied from a cylinder at a pressure greater than atmospheric, whilst in other cases air was being drawn from the atmosphere, the conventional forms of gas metering apparatus were not found to be convenient. Moreover, a continuous range of gas flow from about 100 to 8000 ml. per minute was required. For this reason the following method of gas measurement was devised and it was found to be ideally suited to the desired requirements.

Suppose bottle S is exhausted until the pressure of gas in it is p, the volume of gas in S (at N.T.P.) is then given by

$$V_1 = kp \qquad \text{where } k \text{ is a constant.}$$

Now allow gas to flow into S for a time dt, when the pressure will rise to a value (p + dp) and the volume of gas will then be given by

$$V_2 = k(p + dp)$$

Hence the rate of gas flow over the time dt is given by

$$\frac{V_2 - V_1}{dt} = \frac{dV}{dt} = k.\frac{dp}{dt} .$$

If bottle S is evacuated and gas then allowed to flow through tap d and measurements made of pressure and time it is found, as shown in Fig. 5 for a wide range of gas flow rates, that dp/dt is constant as long as p is less than about 40 cm. of mercury pressure, i.e., for a given setting of tap d, the gas flows at a constant rate into bottle S provided that the pressure in S never rises above 40 cm. of mercury. It is difficult to show why this should be so from a theoretical point of view as the problem of gas flow through a short tube (corresponding to tap d) with a large pressure drop across the ends is an exceedingly complex one and most mathematical treatments neglect turbulence and deal with gases at very low pressures[45].

If S is exhausted to a pressure p_1 the volume of gas it contains at N.T.P. is given by

$$V_1 = V_s.\frac{273}{T}.p_1/76 \text{ ml.}$$

where V_s is the volume of bottle S and T the gas temperature in °A. p_1 is measured in cm. of mercury. Suppose gas is now allowed to flow through tap d into S until a pressure of $p_1 + 20$ is reached (an increase in pressure of 20 cm. was found to be the most convenient for purposes of gas flow calibration), then the volume of the gas in S at N.T.P. is

$$V_2 = V_s.\frac{273}{T}. (p_1 + 20)/76 \text{ ml.}$$

i.e. the change of volume is

$$V_2 - V_1 = V_s . \frac{273}{T} . 20/76 \text{ ml.}$$

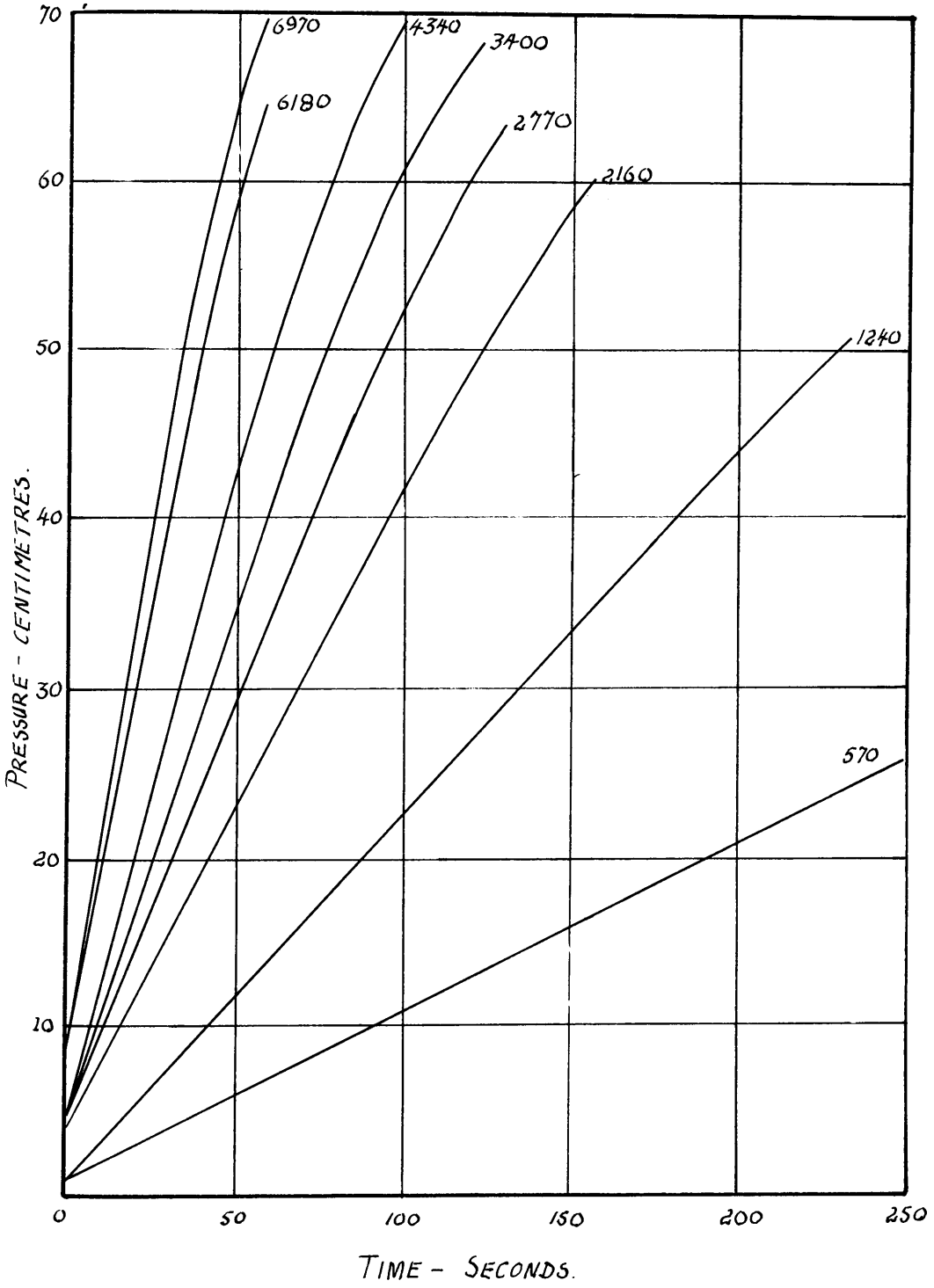

Fig. 5.- Results illustrating the constancy of dp/dt for the gas flow measurement apparatus. The figures on the curves refer to rates of gas flow in ml. per minute.

If the time taken for this 20 cm. rise of pressure is t seconds then, since dp/dt is a constant (for p less than 40 cm.) we may say that the rate of flow is

$$\frac{V_S \cdot 273.20}{T.76.t} \text{ ml/sec.}$$

V_S can be obtained by filling the bottle S with water and weighing, and hence we may express the rate of flow as

$$\frac{K.1}{T\ t} \text{ ml. per second.}$$

where K is a constant which can be readily calculated.

By varying the opening of tap d a chart was constructed of rate of gas flow plotted against the time for an increase in pressure of 20 cm. of mercury, the room temperature T being taken as 295° Å. A small correction was easily made for room temperature variation when reading from this chart and it was found that variations in atmospheric pressure had a negligible effect . The accuracy of this method of gas flow measurement was always within ±1.5 per cent.

During an actual run, gas was drawn continuously through the apparatus, the pressure to the left of taps d and d' (Fig.4) being always less than 40 cm., whereas the pressure on the right hand side was always approximately 76 cm. As there was a pressure drop of about 0.5 cm. from S to the combustion chamber, the manometer M was connected by taps f and k to either one or the other, according to which pressure was being measured at the time. When checking the gas flow rate it was found convenient to isolate the furnace chamber and use pump B for evacuating S.

The furnace used for these combustion experiments is shown in

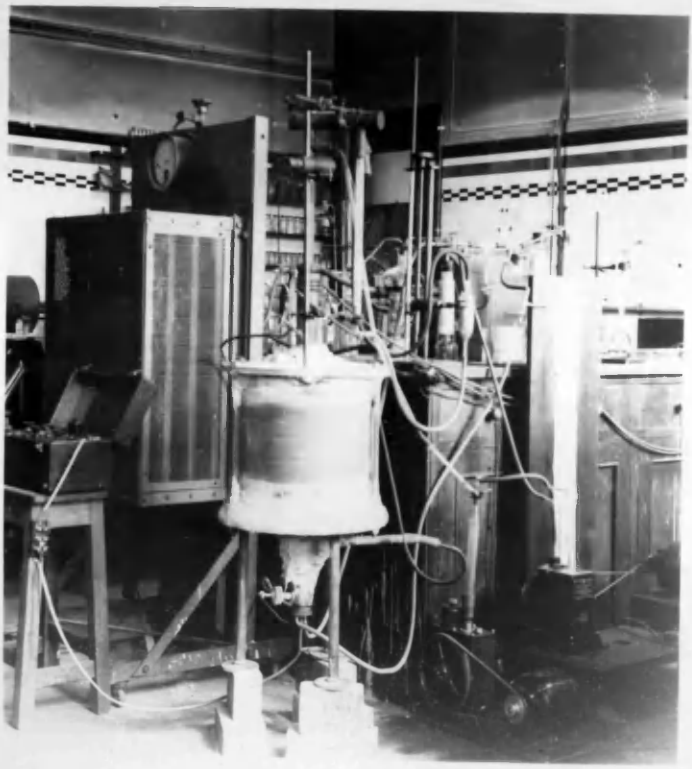

Plate 11.- General view of the combustibility apparatus.

Fig. 6 and a general view of the combustion apparatus is shown in Plate 11. The winding of the molybdenum wound electrical resistance furnace was protected from oxidation by the passage of a continuous stream of cracked ammonia. The latter was produced by passing gaseous ammonia from a cylinder through red hot mullite tubes packed with mild steel turnings. This decomposed the ammonia into its constituent elements which were then passed successively through water, to remove any undecomposed ammonia, sulphuric acid to remove water vapour, and finally granulated zinc to remove any sulphuric acid spray. The combustion chamber itself consisted of a mullite tube (Morgan's Triangle H5 quality) of about 5 cm. internal diameter and it was water cooled at both ends to prevent overheating and burning of the rubber bungs. The gas for combustion was introduced at the bottom and preheated in its passage through three alumina baffle plates drilled with fine holes, these plates being attached to a 9 mm. external diameter closed end mullite tube containing a calibrated platinum/13 per cent. platinum-rhodium thermocouple. In some preliminary experiments with an open ended thermocouple sheath, gas was drawn in-to the furnace over the baffle plates and then back through the sheath and so out of the furnace. In this way the preheated gas was drawn over the bare end of the thermocouple and the results suggested that the gas was actually preheated to the temperature of the combustion chamber. The distance between the top of the thermocouple and the bottom of the burning specimen was 1.0 cm. Great care was taken to wind the furnace in such a way as to produce a uniform hot zone over a length of about 7 cm., the maximum variation along this length being about 10° C. while the temperature variation across a diameter of the furnace tube was less than 3° C.

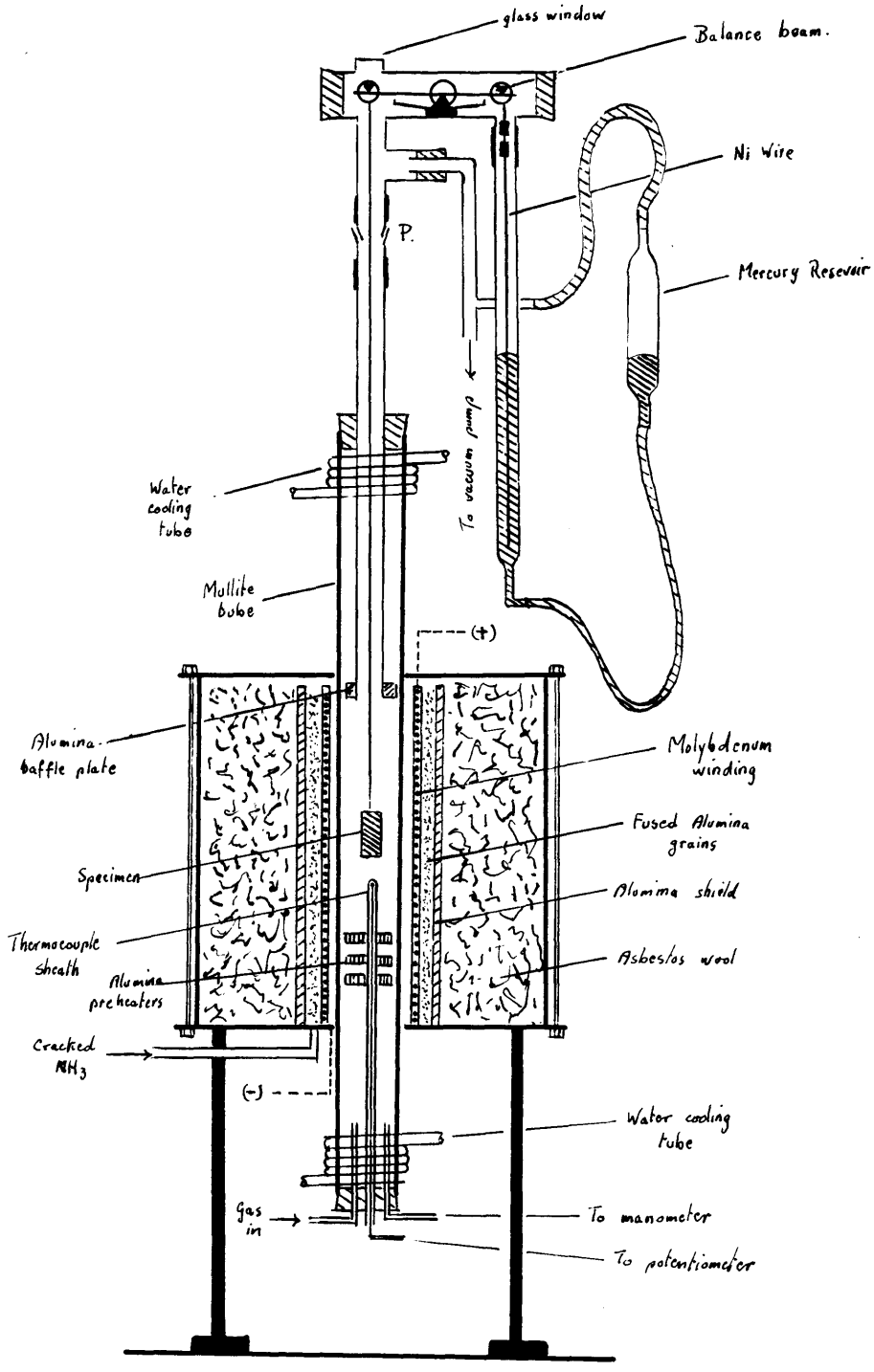

Fig. 6.- The combustion and weighing mechanism.

As experiments were to be conducted under pressures lower than atmospheric and with various gas mixtures, some special form of weighing device was required that could be completely closed off from the atmosphere. Mechanical vacuum balances operated through gas tight seals have been developed but they are unsuitable because of their complexity and the presence in this case of corrosive gaseous products of combustion. Electrical and magnetic attraction devices are likewise unsuitable and in addition the temperature variations near a hot furnace might upset this type of instrument. Several workers in this field have used balances with a low centre of gravity, the displacement from equilibrium being recorded by the reflection of light from a mirror attached to the balance onto a scale or photographic strip[46]. Such methods suffer from the disadvantage that considerable movement of the beam is required for accuracy or the range of the instrument must be restricted, both are undesirable in the present work.

The method of weighing eventually developed is shown in Fig. 6. The specimen was attached to one side of a balance beam (taken from an ordinary laboratory balance) and to the other side was attached a straight length of nickel wire. The cradle of the beam was adjusted so as to restrict its swing, the vertical movement of the nickel wire being reduced to about 0.127 cm. By introducing mercury into the glass tube as shown it was possible to produce an upthrust on the wire and in this way maintain the beam in an equilibrium position. The system was first of all balanced with the specimen in position and the mercury at the bottom of the tube, suitable counterweights being added when necessary. The position of balance was obtained by sighting

a fiducial mark on the wire by means of a telescope. The mercury resevoir was then raised through a known distance with a calibrated screw mechanism; this increased the upthrust on the right hand side (Fig. 6) by a known amount and moved the balance arm from its position of equilibrium. As the specimen burnt away the left hand side of the system became lighter until the beam tilted back to its original position again, the mercury resevoir was again raised and the operation repeated. In this way a record of weight against time could be recorded. The damping effect of the mercury was found to be negligible and surface tension does not introduce any error as it is present as a constant force throughout the whole operation. This apparatus was found to be extremely simple to operate, inexpensive, and very flexible, as by using different gauges of wire any range of weight could be covered. In this particular work a wire of 16 S.W.G. was found to be most suitable. One turn of the screw mechanism raised the mercury resevoir 1.27 cm. corresponding to about 0.25 gm. Hence the maximum movement of the beam (0.127) was equivalent to 0.025 gm. and the total range with a wire of length 40 cm. was equivalent to about 8 gm. The apparatus was calibrated by loading the left hand side with known weights and noting the height of the mercury resevoir required for a balance. Alternatively the calibration could be calculated from the diameter of the wire and the known density of mercury. The first method is to be preferred as it allows for any irregularities in the diameter of the wire whereas the second method used an average figure. Moreover, by calibrating the apparatus by the first method with the furnace running small errors due to temperature variations are reduced to negligible proportions. The whole weighing mechanism

was completely enclosed and a glass window was inserted as shown for centring the specimen in the furnace and also for viewing the progress of combustion. A metal seal at P enabled the whole weighing mechanism to be swung aside for the insertion and removal of the specimen, the wire suspension being disconnected at this point.

The proceedure for a typical combustibility test was as follows. With taps j, i, g, and k closed and e and f open, the bottle S was evacuated with pump B, after which the gas flow was adjusted to the required value as described above. As soon as the furnace was steady at the required temperature taps e and f were closed and k opened and the weighing mechanism lowered into place, after which the whole apparatus was evacuated by means of pump A. The reading of the manometer was noted, g opened, and as soon as the conditions of gas flow became steady, tap h was manipulated to maintain the required pressure in the combustion chamber. The apparatus having been adjusted, pump A was switched off and the apparatus opened at P for the introduction of the previously dried and weighed specimen. The apparatus was then closed, evacuated, and the balance beam adjusted for equilibrium by altering the height of the mercury resevoir; finally after opening tap g a continuous run was made, the mercury resevoir being raised by one turn of the screw mechanism (equivalent to 0.25 gm.) at each step. A complete record of weight, time, pressure and temperature was made throughout the duration of the experiment. It might be noted here that the upthrust on the specimen due to the gas flow was, except in a few cases, negligibly small, but as it remained substantially constant throughout any one run a correction for it was easily made when this became necessary.

An adhering layer of ash was formed on the coke specimens similiar to that described by Finniston in his experiments. This layer was surprisingly stable and it was only when relatively large amounts of gas were drawn past the specimens (in these experiments about 4 litres per minute) that the ash was blown from the surface of the burning coke. Beilby[47] mentions that the ash left on the combustion of wood charcoal leaves a lace-like skeleton which shows the original cell structure of the wood; the same is true of the coke ash in these experiments. When the combustion is carried out at a temperature above that of the ash fusion point, the ash is found to collect into droplets of about 1 to 2 mm. diameter on the surface of the coke. These observations may be summarized by saying that as far as the physical nature of the ash is concerned it does not exist in such a form as would reduce the access of the gas to the burning surface.

CHAPTER IV

COMBUSTION UNDER VARYING CONDITIONS OF GAS FLOW

An account will now be given of experiments carried out in order to investigate the effect of the variables of pressure, linear gas velocity, volume rate of gas flow, gas composition and dimensions of the combustion chamber on the rate of combustion of carbon using the apparatus described in the previous chapter.

Preliminary Experiments

Some preliminary experiments were carried out using electrode arc carbon and pure oxygen, flow rates of up to 10 ml. per second and pressures of 4 to 30 cm. of mercury being employed. If it is assumed that the reaction can be expressed by the equation

$$C + O_2 \longrightarrow CO_2$$

then it will be seen that 1 gm. of carbon requires 1865 ml. of oxygen for complete combustion.

All partially burnt specimens were found to be tapered towards the bottom and two reasons are suggested for this, namely, a decrease in the concentration of oxygen in the gas stream as it passed the specimen and gas turbulence at the lower end of the specimen giving rise to an enhanced rate of reaction. According to Finniston[42] if W is the weight of a specimen after a time t and b the weight of ash in the original specimen then, if the specimen burns symmetrically, it may be shown that

$$\frac{d(W - b)^{1/3}}{dt} \quad \text{is a constant.....(1).}$$

The derivation of this expression assumes that the ash adheres to the partially burnt specimen, if however, it is blown off by the gas stream then a similiar analysis shows that

$$\frac{dW}{dt}^{1/3} \text{ is a constant} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Finniston was able to establish the truth of expression (1) throughout his work thus showing that the rate of combustion was proportional to the superficial surface area of the specimen at any instant as it is from this assumption that Equation (1) is derived. It is interesting in this connection to analyse some results obtained by him for the rate of combustion of specimens of graphite and coke of various shapes and dimensions. Suppose the weight of carbon at any instant is given by $(W - b)$. Then for any given shape

$$A = \beta(W - b)^{2/3}$$

where A is the superficial surface area of the still unburnt part of the specimen and β a shape factor, the specimen being assumed to burn symmetrically. If

$$- d(W - b)/dt$$

is the rate of combustion at time t then we should expect this to be proportional to the true surface area of the carbon and also to some function (say γ) of the gas flow,

$$\text{i.e.,} \qquad - d(W - b)/dt = K\alpha\beta(W - b)^{2/3}.\gamma$$

where α is the ratio of true to superficial surface area and K a constant of proportionally. Hence, rearranging and integrating

$$(W - b)^{1/3} = K\alpha\beta\gamma t/3 + C$$

where $K\alpha\beta\gamma/3$ is Finniston's combustibility "k" and C a constant of integration. For different shapes and dimensions of the same form of carbon burnt under similiar conditions of gas flow and temperature and assuming that the specimen itself does not upset the gas flow appreciably, β will be the only variable in the expression $K\alpha\beta\gamma/3$. Hence if

$$K\alpha\beta\gamma/3 = k$$

then $$k/\beta = K\alpha\gamma/3$$

and k/β will be constant for different shapes of specimen. The calculated values from Finniston's experimental results are given in Table 1. It is seen that the ratio k/β is reasonably constant for similiar experiments conducted at the same temperature thus substantiating the assumption that the rate of combustion is proportional to the superficial surface area of the specimen.

Table 1. Calculated values for k/β from the results of H.M. Finniston.

Experimental Details	Shape	k/β
Manufactured graphite burnt at 925° C.	Cylinder	0.72
Do. but different size of specimen	Cylinder	0.70
Manufactured graphite burnt at 1154° C.	Cylinder	0.91
Do. but different size of specimen	Cylinder	0.88
Coke burnt at 930° C.	Parallelopiped	0.53
Do.	Sphere	0.62
Do.	Cylinder	0.56
Do.	Cylinder	0.62
Do.	Cylinder	0.54

In the present research plots of both $(W - b)^{1/3}$ and $W^{1/3}$ were made against the time t but in neither case was a perfectly straight line relationship obtained as would be expected if Equation (1) or

(2) respectively were valid. This means that the expression

$$\frac{d(W - b)^{1/3}}{dt}$$

was not constant throughout the majority of the time of combustion (even in Finniston's experiments $d(W - b)^{1/3}/dt$ was not constant at the beginning and end of a run where abnormal conditions were prevailing) owing presumably to the fact that the specimen was not burning at a uniform rate over the whole surface, this being the all important assumption for the derivation of the above relationships. For this reason it was decided to investigate the possibilities of using small alumina discs as guards on the top and the bottom of the specimen in order to restrict combustion to the cylindrical surface only. A variety of effects was produced and it was found that by using two discs, one at either end of the specimen, tapering was largely eliminated and the specimen burnt away over the cylindrical surface only although the shielding effect of the discs sometimes caused it to burn more rapidly in the centre than at the ends. Taking this latter case, suppose we assume that the specimen burns uniformly over the cylindrical surface only, then (neglecting the small percentage of ash in the electrode arc carbon which was used for these experiments) if h is the length of the specimen and r its radius, the effective area for combustion is proportional to this surface, i.e., to $2\pi rh$. Hence if the rate of combustion is proportional to this surface area then

$$-\frac{dW}{dt} = \text{Constant} \times r.$$

But the weight of the specimen is

$$W = \text{Constant} \times \pi r^2 h$$

hence

$$W = \text{Constant} \times r^2$$

and $$-\frac{dW}{dt} = \text{Constant} \times W^{\frac{1}{2}}$$

whence by integration

$$W^{\frac{1}{2}} = kt + C \quad \text{where k and C are constants}$$

and this may be compared with the equation

$$W^{1/3} = kt + C$$

which is obtained from (1) when b is zero. When t was plotted against both $W^{1/2}$ and $W^{1/3}$ for specimens burnt with discs at either end it was found that the former led to a more nearly linear relationship over the centre portion of the curve, thus confirming that the rate of combustion was proportional to the superficial surface area of the unshielded part of the specimen.

Although the use of the alumina discs did, in most cases, simplify the problem of uniform combustion (combustion) over the surface of the specimen, their attachment was a tedious procedure as they had to be ground to give a close fit to each individual specimen. In view of this fact and also in the light of the analysis given below it was decided to carry on the work using cylindrical specimens without alumina guards of any kind and the subsequent results suggest that this course was justified.

The relationship of weight of specimen and time during combustion is a curve of the form shown in Fig. 7 (a) and it was in order to obtain a measure of the rate of combustion that Finniston plotted the linear relationship of $(W - b)^{1/3}$ and t. Howevever, as the present work has not shown reliable linearity it was decided to obtain the

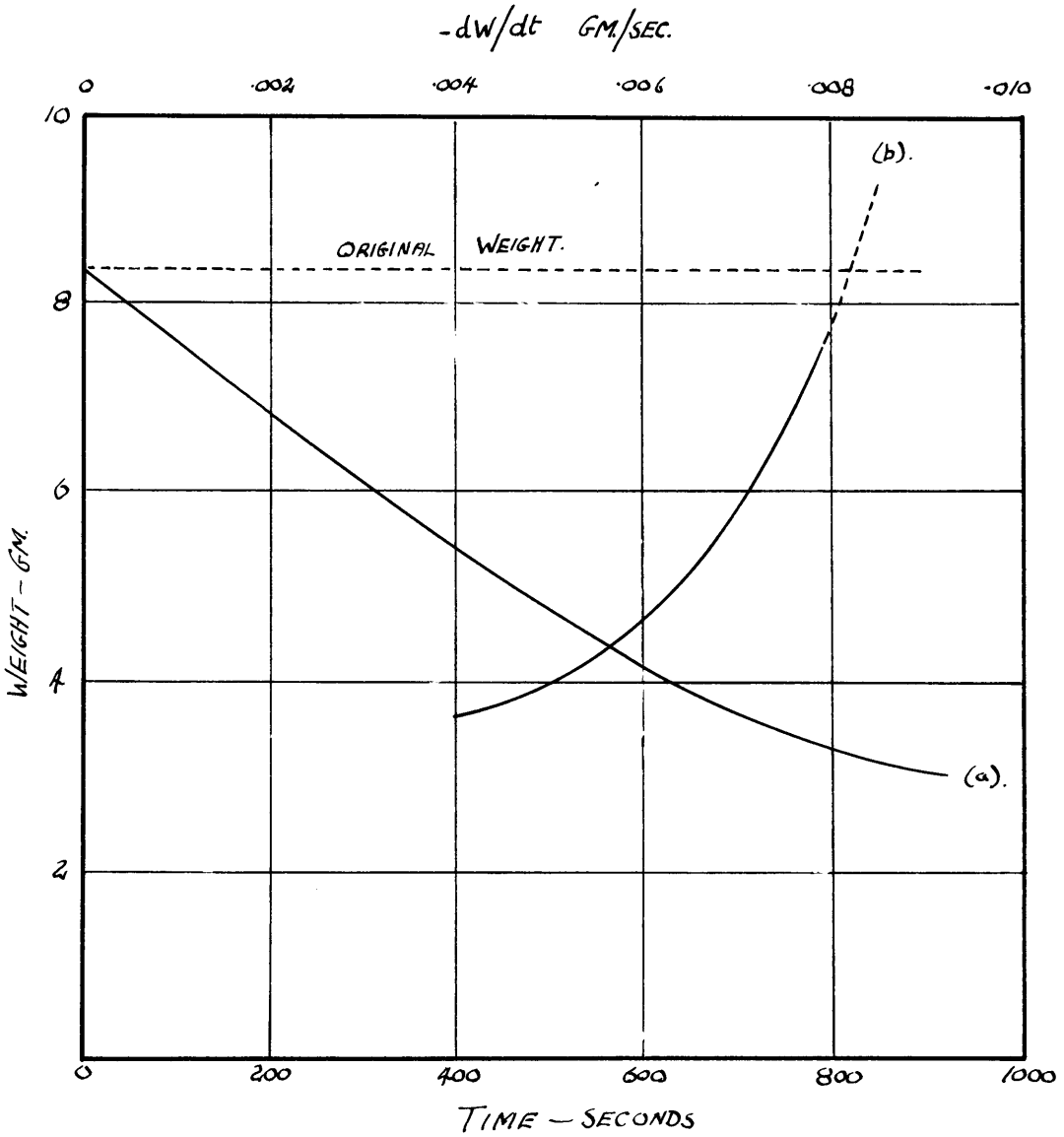

Fig. 7.- Method of plotting combustion results.

rate of combustion dW/dt by taking values of the slope of curve (a) at intervals of 0.5 gm. and plotting these against W as in Fig. 7(b). By extrapolating back to the original weight of the specimen it was possible to obtain a figure for the rate of combustion of a standardized specimen, the results being expressed in gm. per second.

The problem of a differential rate of combustion over the surface of the specimen still remains but it will be shown below that the effect is not so serious as was at first supposed and the figures for each set of experiments are still comparable among themselves.

Analysis of the Combustion of a Single Specimen

The problem of comparing rates of combustion will be considerably simplified if it can be shown that for any one series of experiments, as carried out later on, the effect of a differential reaction rate over the surface of the specimen is such that it may be neglected or if allowance can be made for it.

Let us consider the combustion of a single cylindrical specimen burning in an oxygen containing gas stream as in these experiments, the gas flow being assumed to be streamline. The critical value for the change from streamline to turbulent flow occurs at a value of Reynolds Number, R_e, of about 2000 whereas in this work R_e was generally of the order of 10 and never more than 50. It will be assumed that the reaction equation is given by

$$C + O_2 \longrightarrow CO_2$$

there being an excess of oxygen present. Combustion rates will be considered here in terms of ml. of oxygen (measured at N.T.P.) consumed

per second.

Let V = volume of oxygen supplied per sec. at N.T.P. (ml./sec.).

k = rate of combustion per unit area of surface when unit volume of oxygen passes that surface every second at N.T.P. (ml./sec.).

$a_t = a_b$ = area of top and bottom of cylindrical specimen respectively ($cm.^2$).

a_c = area of cylindrical surface of specimen ($cm.^2$).

h = length of specimen (cm.).

r = radius of cylindrical specimen (cm.).

R_g = total rate of reaction of specimen (ml./sec. of oxygen at N.T.P.).

r_t = rate of reaction of top of specimen (ml./sec. of oxygen at N.T.P.).

r_b = rate of reaction of bottom of specimen (do.).

r_c = rate of reaction of cylindrical surface of specimen (do.).

Let us consider the reduction in volume of the volume V of oxygen as it passes the specimen. After the combustion of the bottom surface the amount of oxygen left is

$$V - r_b$$

and hence the first cylindrical element of the specimen will have a rate of combustion

$$k(V - r_b)\Delta a_c$$

where Δa_c is the area of this first small cylindrical element. Hence the volume of oxygen left after the combustion of the first element will be

$$(V - r_b) - k(V - r_b)\Delta a_c$$

or $$(V - r_b)(1 - k\Delta a_c).$$

Now the rate of combustion of the second cylindrical element

is $$k(V - r_b)(1 - k\Delta a_c)\Delta a_c$$

and the volume of oxygen left will be

$$(V - r_b)(1 - k\Delta a_c) - k(V - r_b)(1 - k\Delta a_c)\Delta a_c$$

$$\text{or } (V - r_b)(1 - k\Delta a_c)^2.$$

Now the rate of combustion of the third cylindrical element is

$$k(V - r_b)(1 - k\Delta a_c)^2\Delta a_c$$

and from analogy with the above expressions it may be said that the rate of combustion of any cylindrical element, say the nth, is

$$k(V - r_b)(1 - k\Delta a_c)^{n-1}\Delta a_c.$$

The total rate of combustion r_c is given by the sum of all such terms the total number of which is

$$a_c/\Delta a_c$$

and this sum is found to be given by

$$r_c \ominus (V - r_b)(1 - e^{-ka_c}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

The rate of combustion of the top surface of the specimen will be given by

$$r_t = (V - r_b - r_c)ka_t \quad \ldots\ldots\ldots\ldots\ldots\ldots (4).$$

and the rate of combustion of the bottom surface is given by

$$r_b = kVa_b = kVa_t \quad (\text{since } a_b \ominus a_t) \quad \ldots\ldots\ldots (5).$$

Hence from equations (3) (4) and (5)

$$R_g = r_b + r_c + r_t$$

$$= V\left\{1 - (1 - ka_b)^2 e^{-ka_c}\right\} \quad \ldots\ldots\ldots\ldots\ldots (6).$$

Rearranging this expression and taking logarithms we obtain

$$\log_e (V - R_g) = \log_e V + 2\log_e(1 - ka_b) - ka_c \quad \ldots\ldots\ldots (7).$$

In order to check the above analysis a series of experiments was carried out in which cylindrical specimens of electrode arc carbon of various lengths were burnt in a stream of air, all other factors being kept constant. Expression (7) can then be written in the form

$$\log_e(V - R_g) = K - ka_c \quad \text{where K is a constant.}$$

But $$a_c = 2\pi rh$$

and hence $$\log_e(V - R_g) = A - Bh \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where A and B are constants, that is, we should expect to find a linear relationship between $\log_{10}(V - R_g)$ and h the length of the specimen. The relevant information in connection with these experiments is given below and the results are shown in Table 2. The latter have been plotted in Fig. 8.

Combustion of electrode arc carbon of ash content 0.5 per cent.

Diameter of combustion chamber 5.15 cm.

Temperature do. 1424° C.

Pressure in do. 8.0 cm.

Volume flow of gas (air) 58.0 ml./sec. (N.T.P.).

Hence volume flow of oxygen, V, 12.2 ml./sec. (N.T.P.).

Linear velocity of gas flow 191 cm./sec.

$a_b = a_c = 2.87$ cm.^{2}

It will be seen that there is a reasonable agreement with theory as far as the linearity of the results is concerned. By extrapolating the results back to h = 0 it is possible to obtain a value of R_g, say R_0 for a specimen of zero length, i.e., an infinitely thin disc.

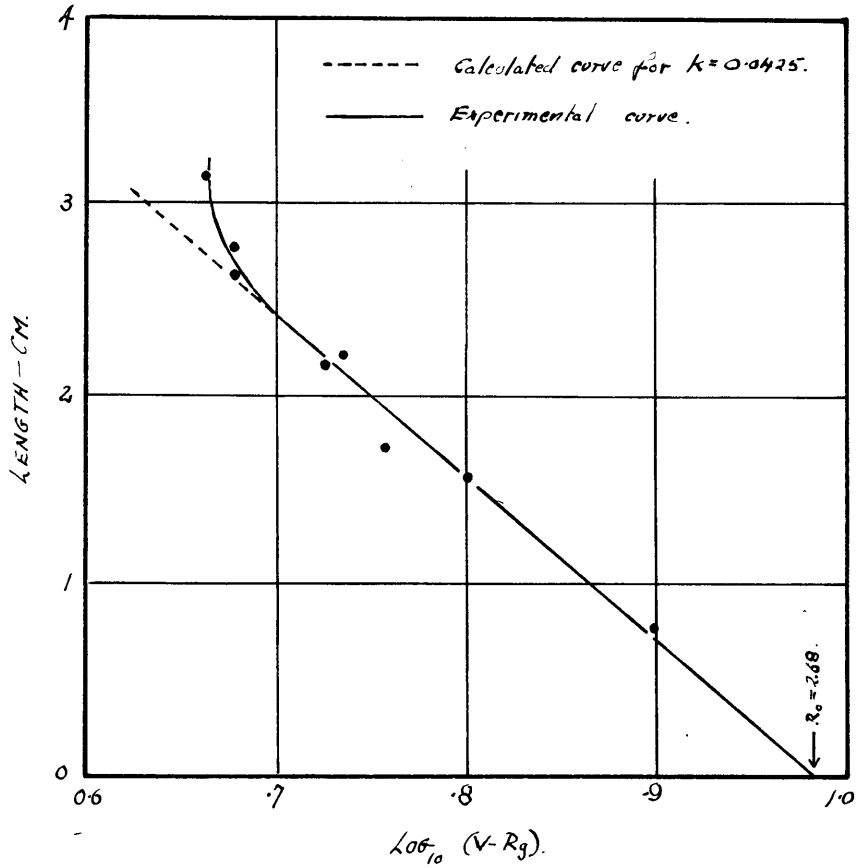

Fig. 8.- A comparison of experimental results with theory for the combustion of specimens of different lengths.

Table 2. Results of burning specimens of different lengths.

h (cm.)	R (gm./sec.) x 10^{-3}	R_g (ml./sec.)	$\log_{10}(V - R_g)$
0.80	2.29	4.28	0.899
1.60	3.16	5.89	.800
1.73	3.48	6.50	.756
2.20	3.72	6.92	.723
2.24	3.66	6.81	.732
2.66	4.00	7.46	.676
2.80	4.00	7.46	.676
3.18	4.08	7.62	.661

By putting a_c equal to zero in equation (6) it is found that

$$R_g = R_0 = 2kVa_b - k^2Va_b^2$$

$$\text{i.e.,} \quad k = \frac{1}{a_b}\left\{1 - \sqrt{1 - \frac{R_0}{V}}\right\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9).$$

Considering the results of Fig. 18 and extrapolating back to h=0, a value is obtained corresponding to R_0 = 2.68 ml. per second. Substituting this value in (9) gives a value for k of 0.0425. Now in the expression (6) since $a_c = 2\pi rh$ it may be written

$$R_g = V\left\{1 - (1 - ka_b)^2 e^{-2\pi rkh}\right\}$$

and by substituting the value of k obtained above the relationship between R_g and h can be calculated. The resulting values obtained in this way have been plotted in Fig. 8 as h against $\log_{10}(V - R_g)$ as shown by the broken line. The fact that the slope of this calculated curve obtained from the extrapolation of the experimental results

agrees so well with the slope of the experimental curve is further evidence in support of the above analysis. The large deviation obtained when h becomes greater than about 3 cm. is almost certainly due to the accumulation of combustion products around the specimen, the above treatment assuming for simplicity that the gas composition is uniform across any horizontal plane, i.e., diffusion in sufficiently rapid to remove the carbon dioxide from the burning surface.

Considering Equation (6)

$$R_g = V\left\{1 - (1 - ka_b)^2 e^{-ka_c}\right\}$$

it is interesting to see how the integrated rate of combustion R_g for the whole specimen varies with k, the rate of combustion per unit area per unit flow of oxygen. Taking the numerical values for the standardized cylinder, i.e., $a_b = 2.87$ cm.^{2} and $a_c = 19.0$ cm.^{2}, values of R_g/V have been calculated for various values of k and the results plotted in Fig. 9. It will be seen that provided R_g/V is less than 0.5, i.e., provided that only half of the total oxygen supplied is actually used up for combustion the variation of R_g with k for a constant value of V is approximately linear or, in other words, the integrated rate of combustion for a whole specimen is proportional to the specific reaction rate per unit area, and this point should be kept in mind throughout the following discussion of results. It should also be noted that the above theoretical treatment remains unaltered if the reaction equation is considered as

$$2C + O_2 \longrightarrow 2CO$$

or any other fixed proportion of CO to CO_2 provided that this remains constant throughout any one series of experiments.

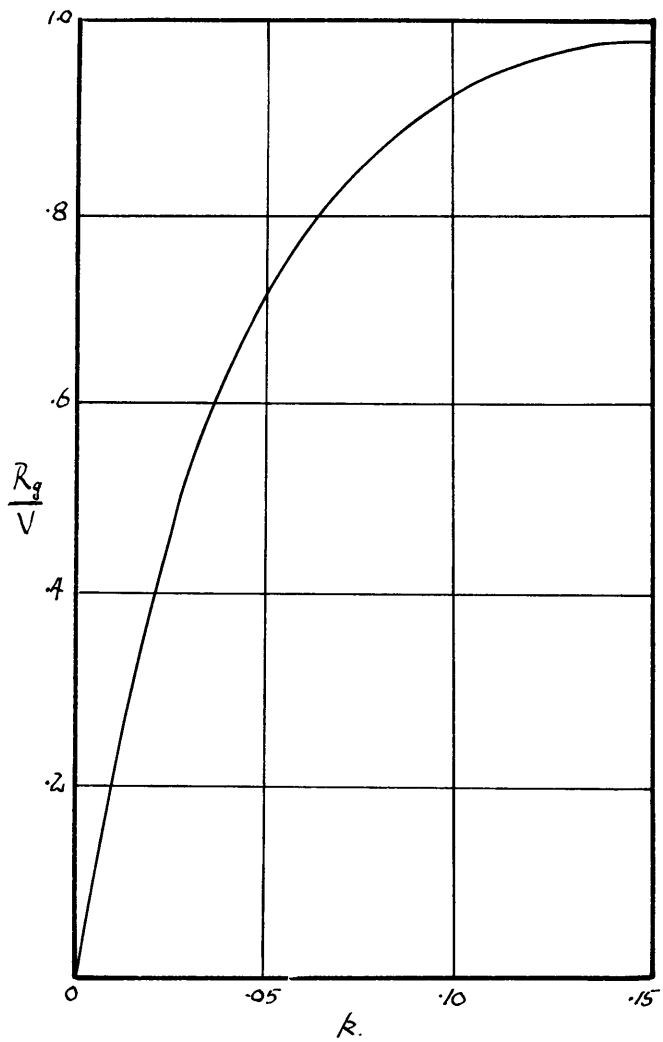

Fig. 9.- A plot of calculated values of Rg/V for various values of k.

Gas Flow and its Effect on Rate of Combustion

It is now proposed to consider the effect of pressure, linear gas velocity, volume rate of gas flow, oxygen concentration, and diameter of combustion chamber on the rate of combustion of both coke and electrode arc carbon. It was soon realised that a simple comprehensive theory was required which would unite these many interdependent variables and enable us to explain the effects observed. The mathematical analysis of the problem by Mayers and others on a basis of fundamental diffusion equations has been mentioned in Chapter 11, but here a more empirical treatment suitable for a wide range of variables will be considered. It will be evident that only those oxygen molecules which can diffuse in towards and make contact with the carbon specimen will be able to react with the carbon surface, and it is on this basis that the problem has been tackled. For the purpose of simplification several assumptions have been made as under.

(1-) For purposes of calculation of gas constants it has been assumed that oxygen is the only gas present and the constants for pure oxygen have been taken in every case. In view of the fact that the values of many of the gas constants at high temperatures are open to doubt in any case it was felt that such a course was justified.

(3) The elementary equations of the classical kinetic theory of gases have been used throughout this treatment.

(3) No assumptions as to the possible chemical nature of the reaction

$$\text{carbon} + \text{oxygen} \longrightarrow \text{combustion products}$$

have been made, but in the absence of data concerning the relative proportions of CO and CO_2 in the resultant reaction products it must

be assumed that the ratio CO/CO_2 is constant throughout any one series of experiments. Moreover a possible increase in the linear gas velocity due to an increase in the volume of the gases in the combustion chamber by a reaction such as

$$2C + O_2(1 \text{ volume}) \longrightarrow 2CO(2 \text{ volumes})$$

will be neglected.

Einstein[49] in a paper dealing with the Brownian movement shows that the mean displacement of a molecule measured linearly from its original position can be given by

$$\bar{x}^2 = 2Dt$$

where $\bar{x}$ is the linear distance traversed in a time t and D is the coefficient of diffusion of the surrounding medium. The simplest formula for the latter due to Meyer is

$$D = \eta/\rho = 1/3.\bar{u}l$$

$$\text{whence} \qquad \bar{x}^2 = 2/3.\bar{u}lt \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18).$$

where η is the coefficient of viscosity of the surrounding gas in poise

$\bar{u}$ is the root mean square velocity of ite molecules in cm./sec.

l is the mean free path of the molecules in cm.

ρ is the gas density in gm./ml.

Suppose we now assume that any oxygen molecule within a distance $\bar{x}$ of the specimen is capable of reaction with the carbon surface whereas any molecule outside this range will be swept out of the combustion chamber before it has an opportunity of diffusing towards and making contact with the specimen. In actual fact the molecules all travel different distances x in a time t, but the distribution

of the values of x is normal with a mean value of $\bar{x}^{50}$. The problem then, is one of finding how much of the oxygen supplied is within the range $\bar{x}$ of the surface of the specimen, all such oxygen being referred to as available oxygen. The c.g.s. system of units will be employed throughout and symbols used previously will be used here.

When gas passes upwards through the annulus between the specimen and the combustion chamber the volume of oxygen available during the time t is given by

$$h(\bar{x}^2 + 2\bar{x}r)S/100$$

where t is the time taken for the gas to traverse the distance h (the length of the specimen), and S is the percentage of oxygen in the gas stream (taken as the percentage of oxygen in the ingoing gas stream).

If p is the pressure in the combustion chamber measured in cm. of mercury and T the temperature in ^{o}A, then the <u>mass</u> of oxygen available is given by

$$M = h(\bar{x}2 + 2\bar{x}r).\frac{S}{100}.\frac{273.}{T}.\frac{p.}{76}.1429.10^{-9} \quad gm.$$

and hence the rate of reaction of the carbon specimen if all this oxygen is used is given by

$$\frac{dM}{dt}.\frac{12{\cdot}01}{32}$$

or if only a proportion of the available oxygen is consumed in the reaction and integrating over the time interval t

Rate of reaction, $R = K\left\{\pi h(\bar{x}^2 + 2\bar{x}r)Sp/Tt \times 1{\cdot}928 \times 10^{-8}\right\}$ gm./sec.....(11).

where K is the proportion of the available oxygen which reacts. The value of t is readily evaluated from a knowledge of the gas temperature, pressure, volume flow rate at N.T.P. and the cross sectional area of the annulus between the combustion chamber wall and the specimen. From this data it is possible to calculate the linear gas flow velocity and hence t since

$$t = \frac{h}{V_1}$$ where V_1 is the linear gas velocity.

The gradual decrease in the value of V_1 throughout the period of combustion does not concern us as all rates of combustion are compared under the initial standardized conditions at the onset of combustion (see p. 25 and also Fig. 7).

It is now proposed to apply the above considerations to each series of experiments in turn, the first series being worked out in full.

Series 1. The Effect of Gas Pressure and Velocity.

It was decided in the first instance to investigate the effect of the two variables gas pressure and linear gas velocity on the rate of combustion. A constant supply of oxygen was drawn past each specimen and by altering the setting of tap h (Fig. 4) it was possible to vary the rate at which gas was drawn from the furnace, thus obtain-different values of gas pressure and velocity. These two variables are related by the expression

$$pV_1 = \text{a constant.}$$

For pressures above 40 cm. (see note on p. 14) a slightly modified method of gas flow measurement was used in which a value of dp/dt was obtained from curves such as those of Fig. 5 for the particular pressure considered. Two series of experiments were carried out, the

first with Norwood coke at 900° C. and the second with Clyde coke at 1350° C. The relevant data and the experimental results are shown below and in Table 3 and the results have also been graphed in Fig. 10.

(a) Combustion of Norwood coke of ash content 8.5 per cent.
Specimen 1.91 cm. diameter and 3.18 cm. in length.
Diameter of combustion chamber 5.08 cm.
Temperature of combustion 900° C.
Volume rate of oxygen flow 12.65 ml. per sec. at N.T.P.
Pressure velocity relationship, $pV_1 = 237$.

(b) Combustion of Clyde coke No. 4V of ash content 13.0 per cent.
Specimen 1.91 cm. diameter and 3.18 cm. in length.
Diameter of combustion chamber 5.36 cm.
Temperature of combustion 1350° C.
Volume rate of oxygen flow 20.2 ml. per sec. at N.T.P.
Pressure velocity relationship, $pV_1 = 459$.

It is now proposed to calculate the value of $\bar{x}$ for Series 1 (a). Considering Equation (10)

$$\bar{x}^2 = 2/3.\bar{u}lt$$

at constant temperature $\bar{u}$ will be constant

$$\text{i.e.,} \quad \bar{x}^2 = \text{Constant} \times lt.$$

Now t will be inversely proportional to the linear gas velocity V_1 and since V_1 is proportional to the gas volume as it passes the specimen

$$V_1 \propto 1/p$$

Table 3. Results of experiments of Series 1 (a) and 1 (b).

(a) Norwood Coke		(b) Clyde Coke	
p (cm.)	R (gm./sec.) x 10^{-3}	p (cm.)	R (gm./sec.) x 10^{-3}
2.0	6.25	2.6	10.2
2.1	6.58	3.0	9.90
4.6	5.81	4.8	9.62
6.4	4.93	10.0	9.62
6.6	5.00	14.0	9.90
7.6	5.29	21.6	9.01
8.8	6.85	23.0	9.17
8.9	6.33	24.0	9.71
11.4	5.59	32.0	9.80
17.0	4.08	43.0	8.62
20.0	6.10	45.0	9.52
27.6	4.88	53.0	9.52
36.0	4.78		
37.0	4.50		
42.0	5.62		
50.7	4.69		

and hence $t \propto p$.

According to the kinetic theory of gases

$$l = \eta \sqrt{\frac{3}{\rho p}}$$

and since η is independent of pressure over the range used in these experiments

$$l = \text{Constant} \times 1/\sqrt{\rho p} .$$

Also the density ρ is proportional to the pressure p

$$\text{i.e.,} \quad l = \text{Constant}/p$$

and combining these equations it is found that

$$\bar{x}^2 = \text{A constant.}$$

It is now necessary to calculate the numerical values of the kinetic quantities involved. For oxygen at N.T.P., $\bar{u} = 4.61 \times 10^4$ cm./sec. and since $\bar{u}$ is proportional to the square root of the absolute temperature, at 900° C. $\bar{u} = 9.56 \times 10^4$ cm./sec. For oxygen at N.T.P., $\rho = 1.43 \times 10^{-3}$ gm./ml., hence at 900° C. and pressure p cm.

$$\rho = 4.38 \times 10^{-6} \times p \quad \text{gm. per ml.}$$

The value of η is calculated from Sutherland's modified equation

$$\frac{\eta_T}{\eta_{273}} = \frac{273 + C}{T + C} \left(\frac{T}{273}\right)^{3/2}$$

where T is the temperature in °Å. and C is Sutherland's Constant.

Taking the values $\eta_{273} = 2.06 \times 10^{-4}$ and C = 127 it is found that at 900° C. $\eta_{1173} = 5.23 \times 10^{-4}$, and hence

$$l = \eta \sqrt{\frac{3}{p}} = \frac{3.75 \times 10^{-3}}{p} \text{ cm.}$$

The value of t is given by $h/V_1 = \frac{3.18}{237} \times p$

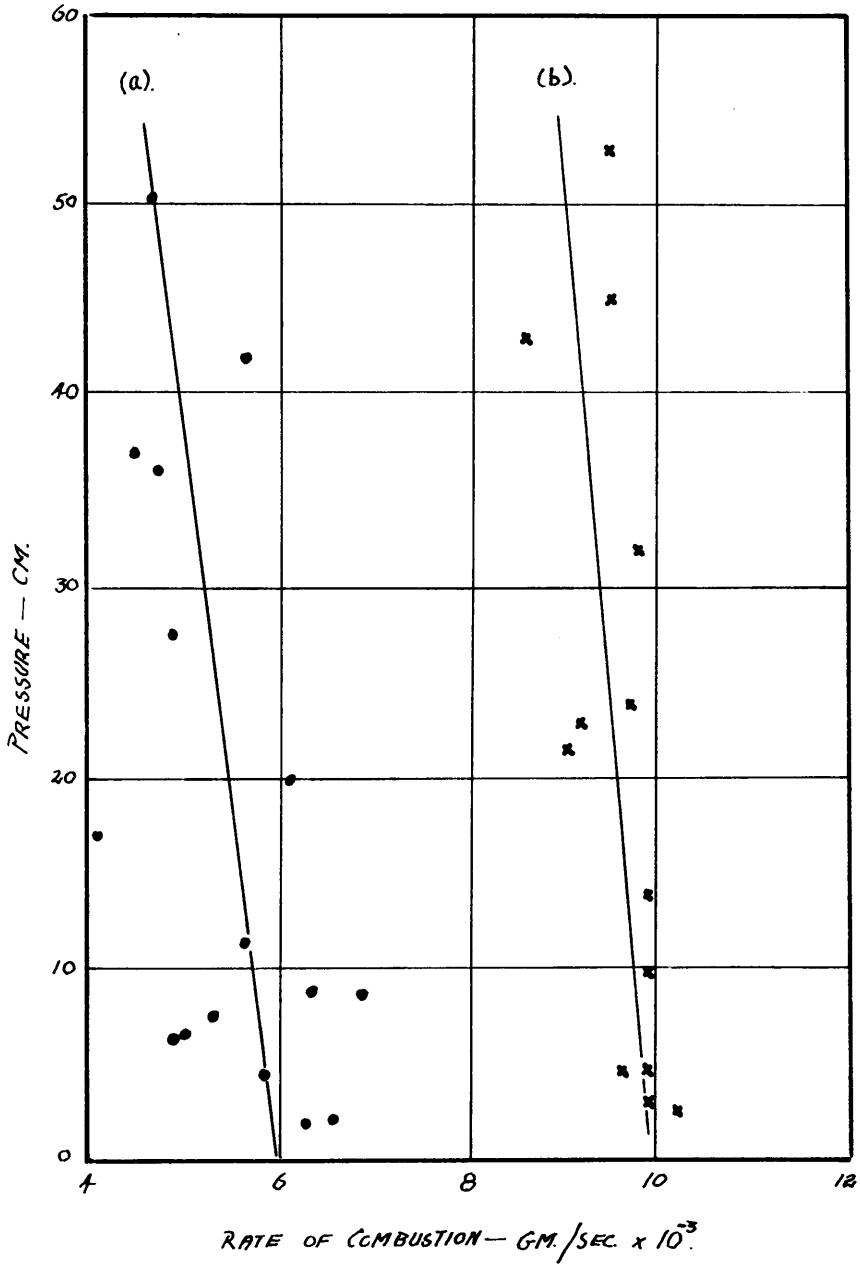

FIG. 10.- Results of experiments of Series 1.

hence $\bar{x} = 2/3.\bar{u}lt = 1.79$ cm.

The corresponding values for Series 1 (b) are found in a similiar manner and the results are compared in Table 4.

Table 4. Calculated values for Series 1.

Calculated Values	Series 1 (a)	Series 1 (b)
$\bar{u} \times 10^{+5}$	0.956	1.12
$\rho \times 10^{-6}$	4.38	3.16
$\eta \times 10^{-4}$	5.32	6.33
$l \times 10^{-3}$	3.75/p	5.34/p
$t \times 10^{-3}$	13.4 x p	6.92 x p
$\bar{x}$	1.79	1.66
(D - d)/2	1.59	1.73

Now it will be seen that in Series (a) $\bar{x}$ is greater than the distance between the surface of the specimen and the wall of the combustion chamber which is given by (D - d)/2, D being the internal diameter of the chamber and d the diameter of the specimen (Fig. 11). For this reason Equation (11) cannot be applied as the assumptions necessary for its derivation imply that once $\bar{x}$ becomes equal to (D - d)/2 all the oxygen molecules are available for reaction and a further increase in $\bar{x}$ cannot give a greater reaction rate. In actual fact many of the oxygen molecules will escape, their displacements, x, being less than the mean $\bar{x}$, and in addition as will be shown in Chapter V, only activated molecules (i.e., molecules endowed with a certain minimum amount of energy) can take part in the reaction. However as $\bar{x}$ approaches the value of (D - d)/2 the above considerations are counteracted to some extent by the effect of deflections of molecules[1]

from the furnace chamber wall. In spite of these complicating factors the important conclusion to be drawn from the above analysis is that x is constant for each series and hence for the same volume flow the rate of combustion would be expected to remain substantially constant irrespective of the linear gas velocity or pressure. The experimental results of Series (b) bear out this conclusion reasonably well as shown in Fig. 10., but the tendency for the rate of combustion to decrease with increase in pressure is more marked in Series (a). No really satisfactory explanation of this discrepancy has been found but it is suggested that the effect of pressure on the ratio of CO to CO_2 might be responsible, a high ratio requiring less carbon for a given volume of oxygen, coupled with the large temperature difference between the two sets of experiments (from 900 to 1350° C.); the equilibrium percentage of CO being greater at the higher temperature.

Series 11. The Effect of Varying Furnace Chamber Diameter.

In an attempt to study the effects of combustion chamber diameter and linear gas velocity on the rate of combustion the annular space surrounding the specimen in the furnace was reduced by the insertion of alumina cylinders, all other factors being maintained constant. These cylinders had of necessity to be a loose fit in the furnace tube to allow for thermal expansion and in order to prevent leakage of gas along the outside of the cylinder a packing of alternate layers of asbestos rope and alumina rings was used as in Fig. 11. It was found impossible to reduce $(D - d)/2$ to less than about 3 mm. as the slightest swaying of the specimen would cause it to touch the cylinder, moreover with a very narrow annular space the upthrust of the gas stream on the

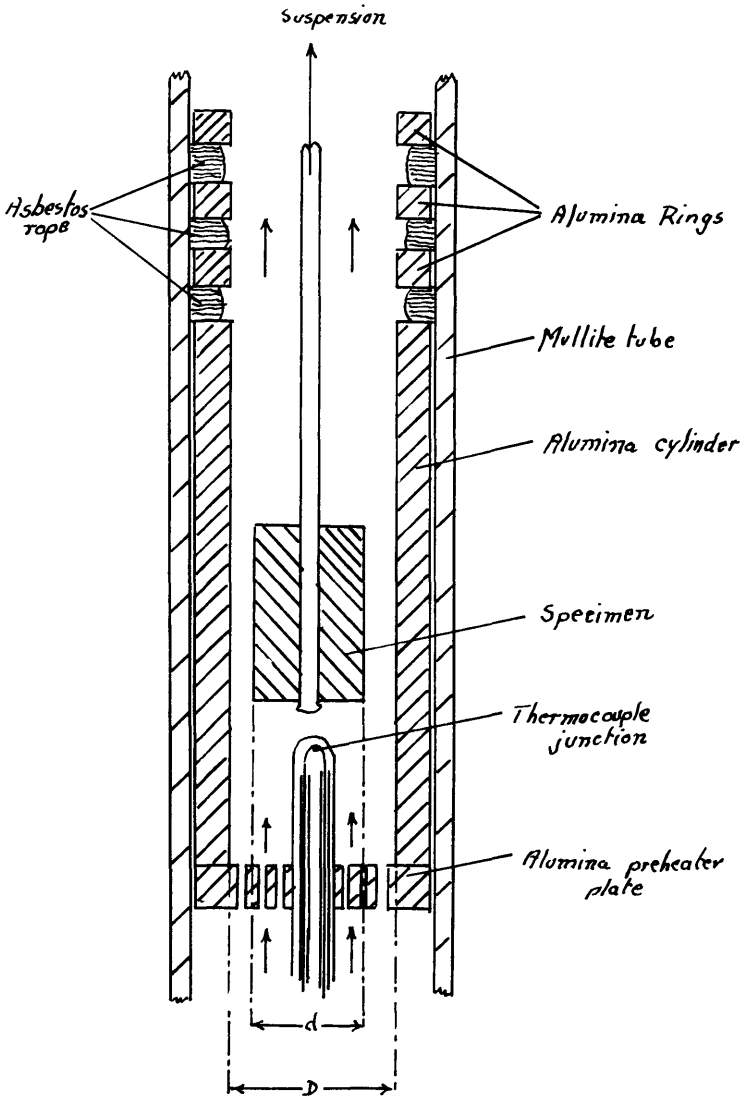

Fig. 11.- Method of varying the furnace chamber diameter by means of the insertion of alumina cylinders.

coke specimen became appreciable and although an approximate correction could be made for this it was not wholly satisfactory. The maintenance of a constant temperature in a confined combustion chamber also presents difficulties on account of the heat liberated during combustion and the low thermal conductivity of the adjacent alumina refractory material. The experimental results are given in Table 5 and they are also plotted in Fig. 12 as rate of combustion against gas velocity V_1, the latter being inversely proportional to the annular area $\pi(D^2 - d^2)/4$ between the specimen and the inner wall of the alumina cylinder. Other relavent information is also given below.

Combustion of Clyde coke No. 1 of ash content 14.6 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Temperature of combustion 900° C.

Volume rate of oxygen flow 11.6 ml. per sec. at N.T.P.

Pressure in combustion chamber 6.7 cm.

Linear gas velocity = 565/annulus area.

$\bar{u} = 6.956 \times 10^{5}$ cm. per sec.

$\rho = 2.93 \times 10^{-5}$ gm. per ml.

$l = 5.60 \times 10^{-4}$ cm.

$\eta = 5.23 \times 10^{-4}$ poise.

$\bar{x} \simeq 5.97\ t = 0.794\sqrt{D^2 - d^2}$.

It will be seen from Fig. 12 that as the annular space becomes larger the linear gas velocity decreases and the rate of combustion also decreases. If the curve is extrapolated back to zero velocity the rate of combustion obtained at this point is equivalent to that of a specimen burning in a stationary atmosphere of infinite diameter.

Table 5. Results of Experiments of Series 11.

V_1 (cm./sec.)	R (gm./sec.) x 10^{-3}	V_1 (cm./sec.)	R (gm./sec.) x 10^{-3}
29.9	5.26	66.6	5.95
29.9	5.21	80.2	6.02
32.3	4.61	80.2	6.37
32.3	4.93	128	7.00
56.0	6.10	132	7.41
59.2	7.19	250	7.46
66.6	6.67	250	7.94

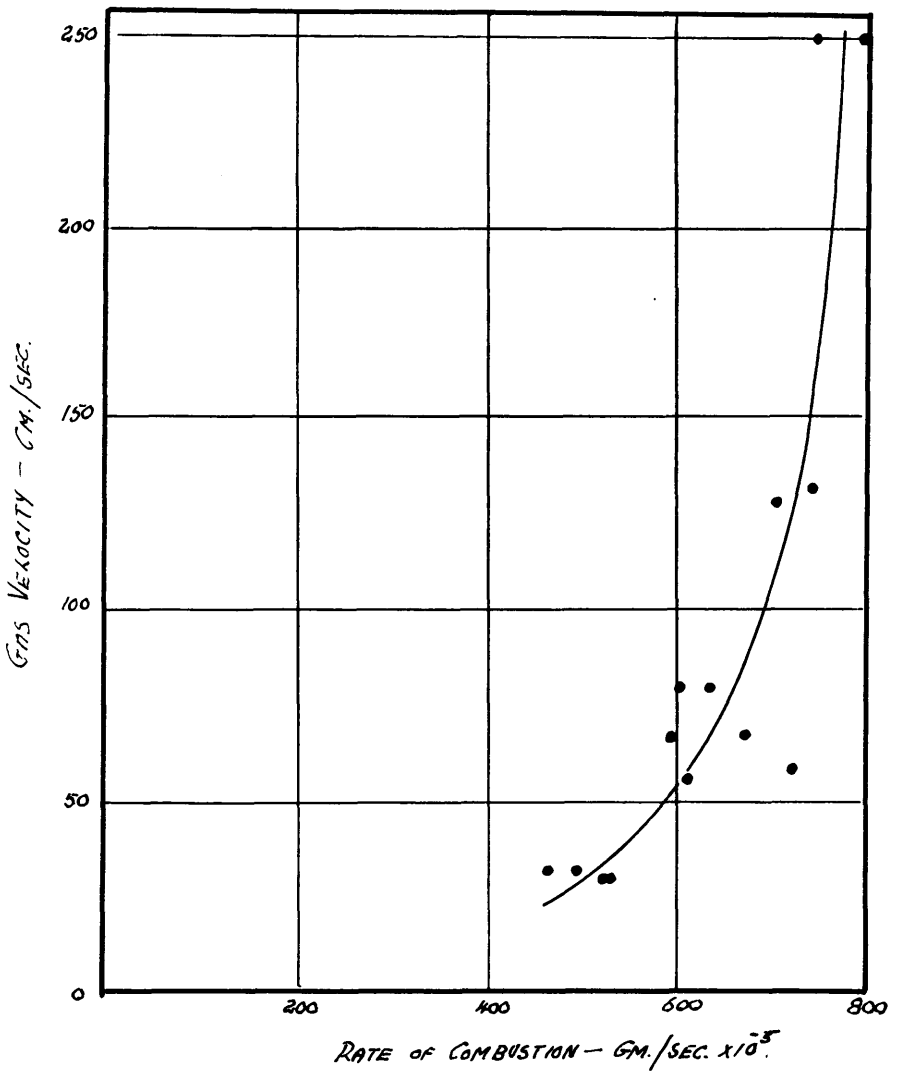

Fig. 12.- Results of experiments of Series 11.

By writing $\bar{x}$ in the form

$$\bar{x} = 0.794(D - d)\sqrt{\frac{D + d}{D - d}}$$

it is seen that $\bar{x}$ is always greater than $(D - d)/2$ and hence similiar remarks will apply here to those expressed for Series 1 (a). However, in this case, as the annular area is decreased, i.e., as the linear gas velocity becomes greater, the ratio of $\bar{x}$ to $(D - d)/2$ increases and hence the rate of combustion would be expected to increase owing to the greater number of oxygen molecules reflected from the walls of the combustion chamber and this is actually seen to be the case in Fig. 12. It may be noted that assuming the combustion reaction is

$$C + O_2 \longrightarrow CO_2$$

the maximum possible rate of combustion is 6.22×10^{-3} gm. per sec. and as many of the experimental rates of combustion are greater than this some carbon monoxide must be formed by a reaction such as

$$2C + O_2 \longrightarrow 2CO.$$

Series 111. The Effect of Varying the Gas Volume at Constant Pressure.

Another method of varying the linear gas velocity is to alter the volume flow rate of gas, maintaining the pressure constant, i.e., the gas velocity then varies in direct proportion to the volume of gas used for the experiment. Three series of experiments were performed, two using coke and the third with electrode arc carbon, the pressure being maintained at a constant value throughout each series by altering the setting of tap h (Fig. 4) for each new rate of gas flow. Air was used in these experiments in place of oxygen. The relevant data in connection with each series is given below together with the results in Table 6. The latter have been plotted in Fig. 13 on a basis of

oxygen supplied per second (air contains 21 per cent. of oxygen by volume).

(a) Combustion of Yorkshire coke of ash content 12.3 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Temperature of combustion 1200° C.

Diameter of combustion chamber 5.08 cm.

Pressure in combustion chamber 11.4 cm.

(b) Combustion of Clyde coke No. 11 of ash content 14.2 per cent.

Specimen 1.91 cm. diameter and 3.18 cm . in length.

Temperature of combustion 1200° C.

Diameter of combustion chamber 5.08 cm.

Pressure in combustion chamber 13.3 cm.

(c) Combustion of Electrode Arc Carbon of ash content 0.5 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Temperature of combustion 1427° C.

Diameter of combustion chamber 5.15 cm.

Pressure in combustion chamber 8.1 cm.

It will be seen from Fig. 13 that the use of electrode arc carbon leads to far less scatter of results on account of its homogeneous composition and physical characteristics as compared with commercial blast furnace coke.

The calculated quantities required for the evaluation of x are given in Table 7. W_o in this Table is the volume rate of oxygen flow measured in ml. per sec. at N.T.P. The three equations for rate of combustion R as calculated from these values by means of Equation (11)

Table 6. Experimental Results of Series 111.

(a) Yorkshire Coke		(b) Clyde Coke No. 11		Electrode Arc Carbon	
Vol. O_2 ml./sec.	R (gm./sec.) x 10^{-3}	Vol. O_2 ml./sec.	R (gm./sec.) x 10^{-3}	Vol. O_2 ml./sec.	R(gm./sec.) x 10^{-3}
10.4	3.39	13.4	3.48	1.08	0.76
11.5	3.53	13.6	3.33	1.08	0.83
11.8	3.23	15.0	3.26	2.33	1.50
12.6	3.18	16.6	3.75	2.33	1.41
13.4	3.31	16.9	3.13	5.07	2.47
14.3	3.55	17.2	3.37	5.07	2.65
15.7	3.70	18.4	3.50	8.25	3.49
14.3	3.48	18.7	3.65	8.25	3.38
16.5	3.83	19.0	3.46	11.6	3.92
17.0	3.85	21.6	3.52	11.6	4.13
18.0	3.69.	22.5	4.03	14.9	4.33
18.4	4.24	22.9	3.80	14.9	4.29
18.7	4.05			20.0	5.00
19.2	4.47			20.0	4.91

are given below together with the value of W_o for which $\bar{x} = (D - d)/2$. As emphasized previously, these equations are only valid so long as $\bar{x}$ is less than $(D - d)/2$, i.e., as long as W_o is greater than the limiting value given below.

Table 7. Calculated values for Series 111.

Values Calculated	Series 111 (a)	Series 111 (b)	Series 111 (c)
$\bar{u} \times 10^5$	1.07	1.07	1.15
$l \times 10^{-4}$	4.21	3.61	6.92
$\rho \times 10^{-5}$	3.97	4.64	2.45
$\eta \times 10^{-4}$	5.98	5.98	6.50
t	$0.324/W_o$	$0.378/W_o$	$0.209/W_o$
$\bar{x}$	$3.12/\sqrt{W_o}$	$3.12/\sqrt{W_o}$	$3.30/\sqrt{W_o}$
$(D - d)/2$	1.59	1.59	1.62

Equations for the rateof combustion as calculated from Equation (11).

(a) $R = K(0.937 \times 10^{-3} + 0.574 \times 10^{-3}\sqrt{W_o})$

(b) $R = K(0.941 \times 10^{-3} + 0.575 \times 10^{-3}\sqrt{W_o})$

(c) $R = K(1.02 \times 10^{-3} + 0.591 \times 10^{-3}\sqrt{W_o})$

Minimum values of W_o for which these equations are valid:

(a) $W_o = 3.85$ ml. per sec.

(b) $W_o = 3.85$ ml. per sec.

(c) $W_o = 4.16$ ml. per sec.

By substituting appropriate values of W_o in Equations (a) (b) and (c) above it is possible to obtain calculated graphs of R against W_o. By choosing suitable values of K (a different one for each series)

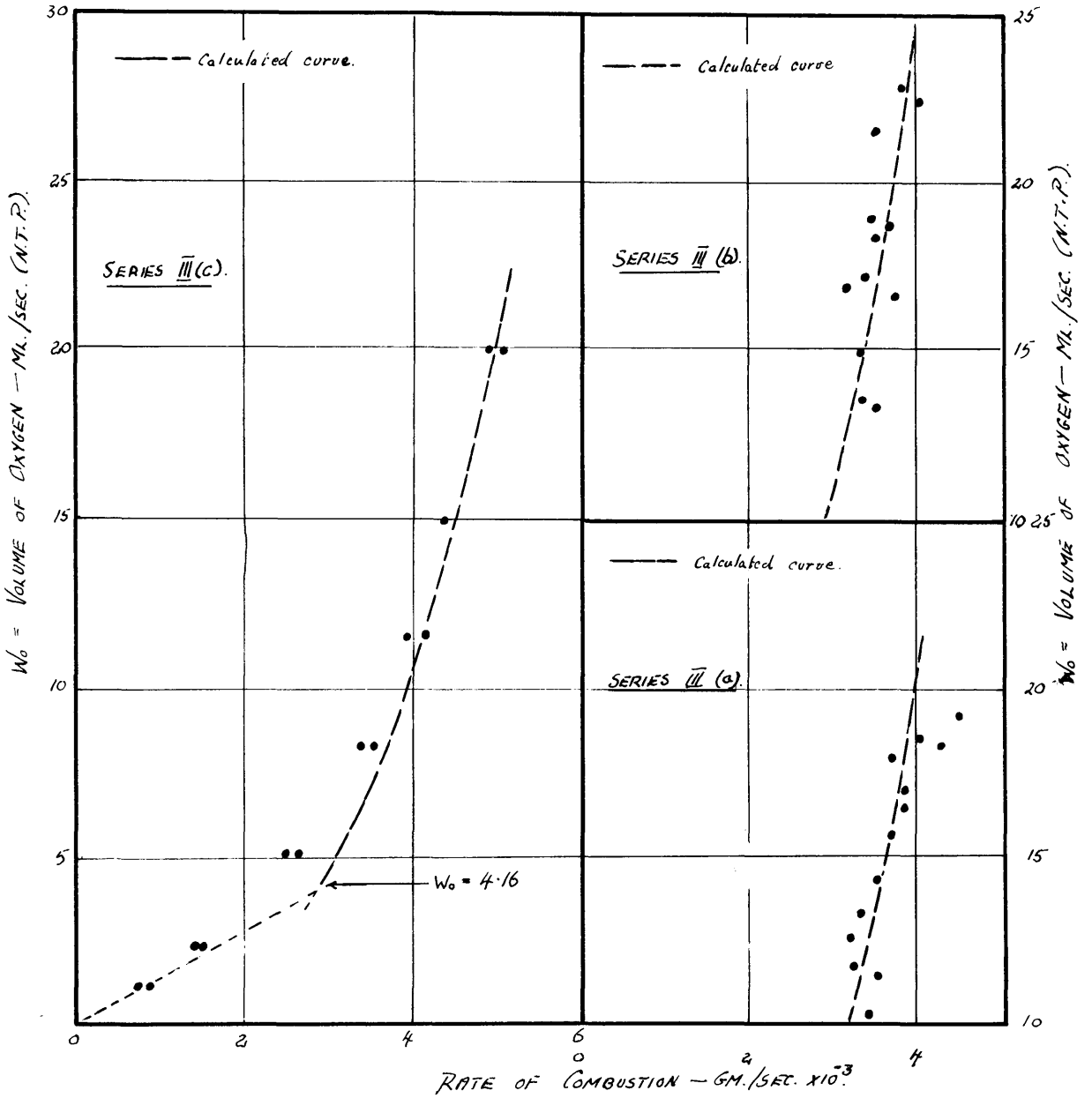

Fig. 13.- Comparison of experiment and theory for Series 111.

the calculated values of R (Table 8) are seen to fit the experimental points reasonably well in the range where $\bar{x}$ is less than (D - d)/2 as shown in Fig. 13. The value of the constant K was chosen by a process of trial and error so as to give values of R of the right magnitude; the important point about the calculated equations above is that they give curves whose slopes fit the experimental results.

Table 8. Calculated combustion rates for Series 111.

W_o ml./sec.	(a)	(b)	(c)
	R gm./sec. $\times 10^{-3}$ K = 1.14	R gm./sec. $\times 10^{-3}$ K = 1.05	R gm./sec. $\times 10^{-3}$ K = 1.35
5	2.42	2.22	3.16
10	3.14	2.88	3.91
15	3.60	3.30	4.47
20	4.00	3.67	4.95
25	-	-	5.38

In Series 111 (c) when W_o becomes less than 4.16 ml. per second, $\bar{x}$ becomes greater than (D - d)/2 and there is a discrepancy between the slopes of the calculated and experimental curves in this region. Since for the values of $\bar{x}$ greater than (D - d)/2 all the molecules of gas are able to reach the specimen (according to the theoretical treatment used here) it will be seen that the rate of combustion would be expected to be proportional to the amount of oxygen supplied and this may be represented by drawing a straight line from the point W_o = 4.16 to the origin in Fig. 13 (c).

Series 1V, V and V1. Experiments at Constant Linear Gas Velocity.

Having shown that the effect of altering the linear gas velocity

is essentially one of altering the magnitude of $\bar{x}$ and hence the volume of available oxygen, it was decided to carry out experiments in such a way that the amount and pressure of the gas could varied whilst the linear gas velocity was kept constant.

In Series IV experiments were carried out in which the diameter of the combustion chamber was varied by using alumina cylinders as before but in this case the total volume flow of gas was also varied in such a way as to maintain a constant linear gas velocity. In addition, the proportion of oxygen in the gas supplied was varied so that the total rate of oxygen flow into the combustion chamber was the same in all cases. The percentage of oxygen in the ingoing gas stream was thus inversely proportional to the annulus area $\pi(D^2 - d^2)/4$ of the combustion chamber, for if the annulus area was say doubled, the total volume of gas had also to be doubled to maintain a constant linear gas velocity (the pressure being kept constant) and hence the percentage of oxygen had to be halved in order to provide a constant volume of oxygen. Two series of experiments were carried out along these lines the relevant data being given below and the results in Table 9. The latter are plotted in Fig. 14 and the curves may be extrapolated back to the origin since at zero percentage of oxygen the rate of combustion must be zero.

(a) Combustion of Clyde coke No. 11 of ash content 14.2 per cent.
Specimen 1.91 cm. diameter and 3.18 cm. in length.
Temperature of combustion chamber 1200° C.
Pressure in combustion chamber 13,2 cm.

Linear velocity of gas flow 193 cm. per sec.

Volume flow rate of oxygen 14.0 ml. per sec. at N.T.P.

(b) Combustion of Clyde coke No. 111 of ash content 13.9 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Temperature of combustion chamber 1300° C.

Pressure in combustion chamber 13.2 cm.

Linear velocity of gas flow 206 cm. per sec.

Volume flow rateof oxygen 14.0 ml. per sec. at N.T.P.

Table 9. Experimental results of Series IV.

(a) Clyde Coke No. 11		(b) Clyde Coke No. 111.			
R (gm./sec.) x 10^{-3}	Oxygen %	R (gm./sec.) x 10^{-3}	Oxygen %	R (gm./sec.) x 10^{-3}	Oxygen %
2.09	11.4	3.31	11.3	6.38	30.1
4.88	23.6	2.94	11.3	7.81	50.7
5.95	30.3	3.13	11.3	8.33	50.7
8.00	51.0	5.35	23.5	9.35	63.3
8.77	63.9	5.08	23.5	9.09	63.3
9.80	82.1	6.78	30.1	-	-

The calculated values for the determination of $\bar{x}$ are given in Table 10. By means of Equation (11) the rate of combustion R has been calculated from these figures for each series, viz.,

(a) $R = K(1.75 \times 10^{-4} \times S)$ gm. per sec.

(b) $R = K(1.79 \times 10^{-4} \times S)$ gm. per sec.

where S is the percentage of oxygen in the gas supplied. It is seen from this that a linear relationship is to be expected between the rate of combustion and the percentage of oxygen in the gas

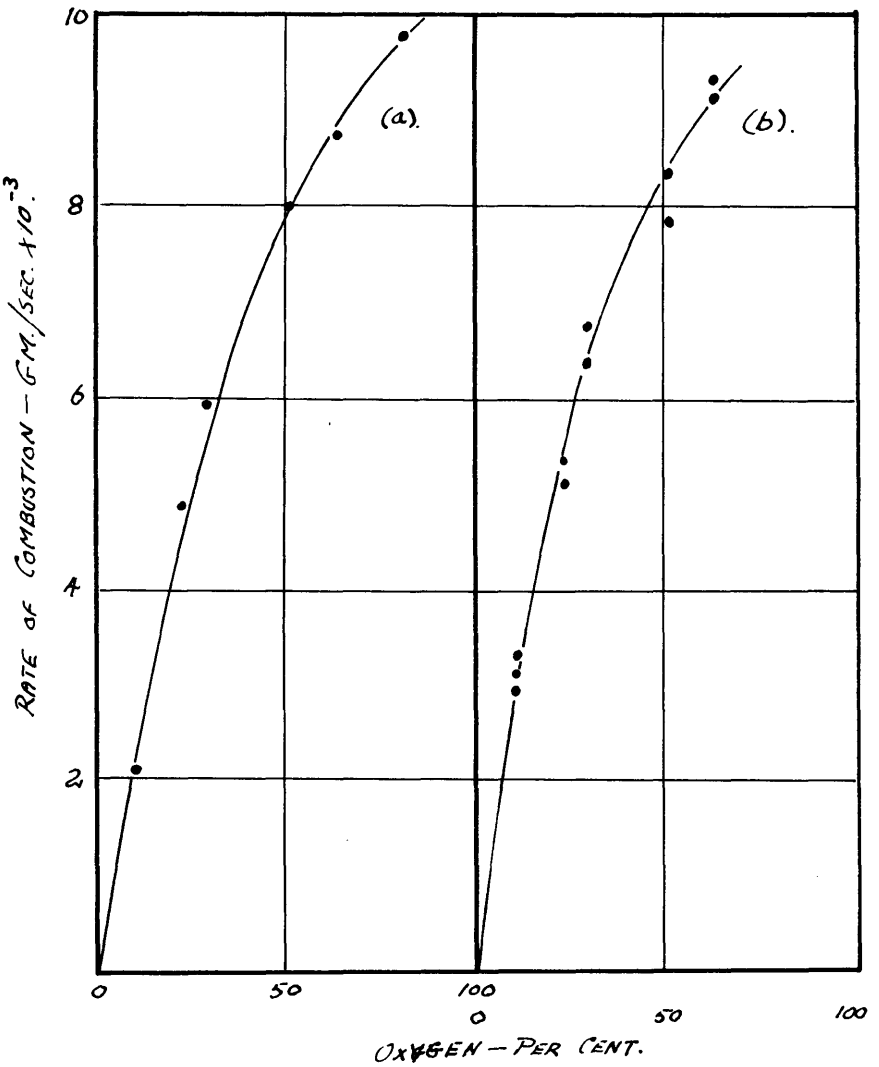

Fig. 14.- Experimental results of Series IV.

stream. However, this will only be true as long as

$$\bar{x} \leqslant (D-d)/2.$$

Now since the value of S is inversely proportional to the annulus area it is possible to calculate the value of S for which

$$\bar{x} = (D - d)/2$$

and the above equations will be true only for values of S less than this calculated figure which has the value 42.8 per cent. for Series IV (a) and 41.6 per cent for Series IV (b). Taking values of K of 1.51 and 1.09 in (a) and (b) respectively it will be seen from Fig. 14 that this linear relationship holds in both (a) and (b) up to about 25 to 30 per cent of oxygen as compared with the calculated value of about 42 per cent. However, considering the simplicity of the calculations the agreement with theory is encouraging. Once $\bar{x}$ becomes greater than (D - d)/2 the rate of combustion increases owing to the deflection of molecules from the combustion chamber wall i.e., the conditions become somewhat similiar to the analogous cases in Series II and III.

Table 10. Calculated values for Series IV.

Values Calculated	Series (a)	Series (b)
$\bar{u} \times 10^{5}$	1.07	1.11
$\rho \times 10^{-5}$	4.59	4.30
$\eta \times 10^{-4}$	5.98	6.22
$l \times 10^{-4}$	3.64	3.91
$t \times 10^{-2}$	1.65	1.54
$\bar{x}$	0.66	0.67
K	1.51	1.09

Series V.

This series of experiments was similiar to the last except that in this case the gas composition was maintained constant, air being used in each case, but the total volume of air supplied and the annulus area were still varied in such a way as to ensure a constant linear gas velocity for each experiment. It was found that when the annulus area exceeded a certain value the rate of combustion became constant and such a result would be expected from the arguement put forward below. The experimental results are given in Table 11 and they are graphed in Fig. 15 the curve being extrapolated back to the origin for, with an infinitely small annulus area, the amount of gas required will be infinitely small (if the linear gas velocity is to remain constant) and hence the rate of combustion will tend towards zero.

Combustion of Clyde coke 111 of ash content 13.9 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Temperature of combustion chamber 1300° C.

Pressure in combustion chamber 13.1 cm.

Linear velocity of gas flow 210 cm. per sec.

$\bar{u} = 1.11 \times 10^{5}$ cm. per sec.

$\rho = 4.27 \times 10^{-5}$ gm. per ml.

$\eta = 6.22 \times 10^{-4}$ poise.

$l = 3.95 \times 10^{-4}$ cm.

$t = 1.51 \times 10^{-2}$ sec.

$\bar{x} = 0.66$ cm.

$K = 0.63$

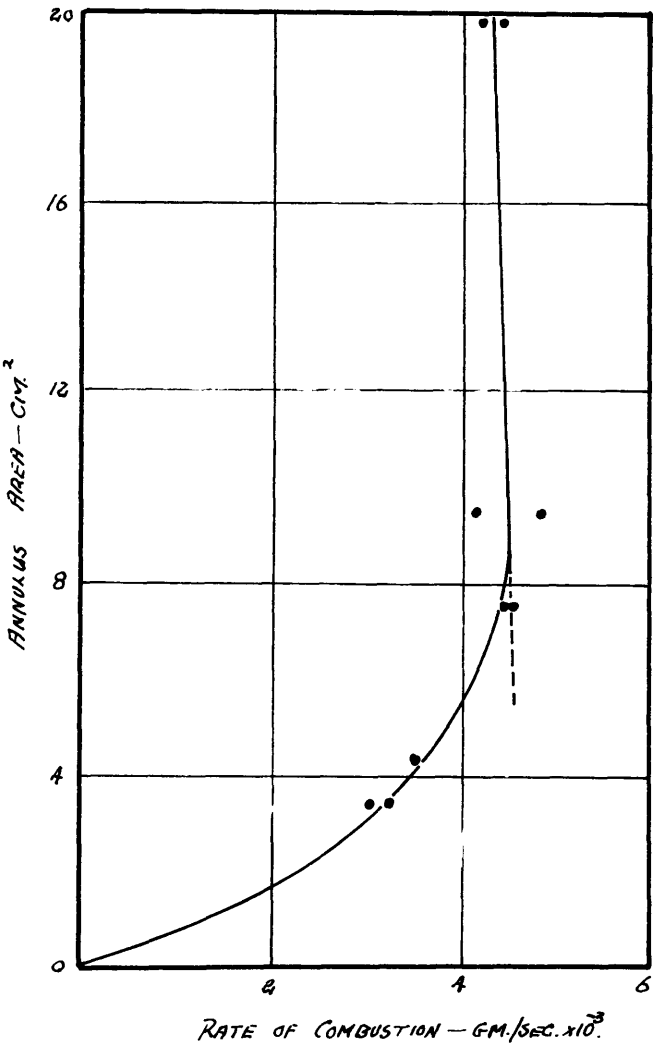

Fig. 15 Results of experiments of Series V.

Table 11. Experimental results of Series V.

$R \times 10^{-3}$ gm./sec.	3.02	3.21	3.50	4.55	4.46	4.17	4.83	4.41	4.20
Annulus Area cm.^{2}	3.53	3.53	4.41	7.50	7.50	9.53	9.53	19.8	19.8

Using Equation (11) the rate of combustion is found to be

$$R = 3.82 \times 10^{-3} \times K \text{ gm. per sec.}$$

i.e., the rate of combustion is constant as long as $\bar{x}$ is less than $(D - d)/2$. When $\bar{x} = (D - d)/2$ it is found that the value of the annulus area $\pi(D^2 - d^2)/4$ is equal to 5.37 cm.^{2}, hence as long as the annulus area is more than 5.37 cm.^{2} the rate of combustion is expected to be constant. That this is actually the case is shown in Fig. 15, the value of K for the straight portion of the curve being about 1.15. This series of experiments is perhaps the most significant of all in that it shows clearly that no matter how big the combustion chamber or how much gas is passed through, the limiting factor as regards rate of combustion is the value of x which determines the volume of exygen that is actually available for combustion in the limited time available. Comparing Series 11 with Series V, it is seen that in both cases the annulus area of the combustion chamber is varied in order to study its effect on the rate of combustion. However, at the time of the experiments of Series 11 the full significance of the quantity x was not appreciated and it is only when this factor is taken into account that the reason for the difference between Figs. 12 and 15 becomes apparent. The essential difference between Figs this series and the previous one is that the oxygen concentration in the gas in this case is kept constant. Hence, although in each case a constant volume of gas is available (so long as $x \leqslant (D - d)/2$), in the previous case of Series 1V the

oxygen concentration was varied so that the rate of combustion was then proportional to the percentage of oxygen in that constant volume.

Series VI

A series of experiments similiar to those described under Series III was carried out using pure oxygen. However, in this case the tap h of the evacuation pump (Fig. 4) was not altered so the linear gas velocity remained constant but the pressure increased in direct proportion to the volume of oxygen used. (Slight adjustment of h was necessary as the efficiency of the pump varied a little with the pressure of the gas being removed.). The relevant data and the results are given below and in Table 12 and they are also graphed in Fig. 16.

Combustion of Clyde coke III of ash content 13.9 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Diameter of combustion chamber 5.35 cm.

Temperature of combustion chamber 1300° C.

Linear velocity of gas flow 114 cm. per sec.

Relationship between oxygen supply and pressure $W_o = 5.13p$.

$\bar{u} = 1.11 \times 10^{5}$ cm. per sec.

$\rho = 3.26 \times 10^{-6} \times p$ gm. per ml.

$\eta = 6.22 \times 10^{-4}$ poise.

$l = 5.16 \times 10^{-3}/p$

$t = 2.79 \times 10^{-2}$ sec.

$x = 3.26/p$ cm.

$(D - d)/2 = 1.72$

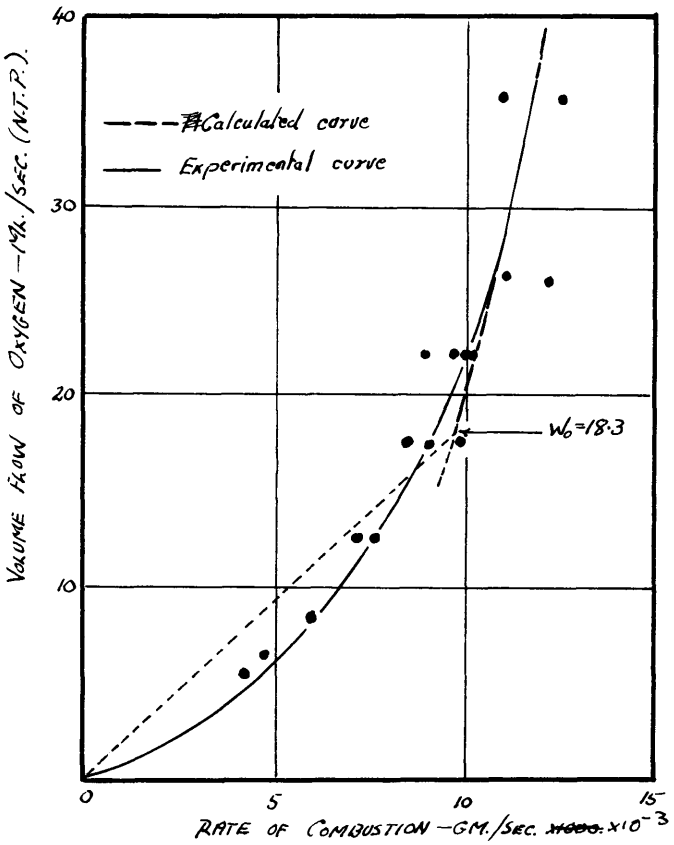

Fig. 16.- Results of Experiments of Series V1.

Table 12. Results of experiments of Series V1.

R (gm./sec.) x 10^{-3}	W_o	R (gm./sec.) x 10^{-3}	W_o
4.17	5.60	8.85	22.3
4.76	6.60	9.62	22.3
5.99	8.37	10.2	22.5
7.19	12.9	10.1	22.5
7.58	12.9	12.2	26.1
9.00	17.7	11.0	26.5
9.90	17.9	10.9	36.0
8.47	17.9	12.5	36.0

The rate of combustion calculated from Equation (11) is found to be

$$R = K(0.468 \times 10^{-2} + 2.75\ p \times 10^{-3}) \text{ gm. per sec.}$$

where p is the pressure in the combustion chamber. This equation is valid only so long as $\bar{x} \leqslant (D - d)/2$. When $\bar{x} = (D - d)/2$ the value of p can be calculated and hence the value of W_o the volume of oxygen supplied every second. This is found to be 18.3 ml. per sec. and hence the above reaction equation is valid only as long as $W_o \geqslant 18.3$. By putting values of p in the equation above and using a suitable value for K (in this case K = 0.98) the value of R may be calculated and a calculated curve drawn as in Fig. 16.

when W_o = 20 25 30 35 40

R = 9.9 10.5 11.0 11.6 12.1

It will be seen that so long as $W_o \geqslant 18.3$ there is reasonably good agreement between the slopes of the calculated and experimental curves. For smaller values of W_o a similiar arguement may be used

to that on p. 46 and a straight line drawn from the point W_o = 18.3 to the origin.

Series V11

Before concluding these experiments it was decided to investigate the effect of oxygen concentration on the rate of combustion, all other factors being kept constant. Using mixtures of oxygen and air combustion measurements were carried out over a range of oxygen concentration varying from 21 to 100 per cent. for an electrode arc carbon and from 21 to 59 per cent for a coke. As was expected the rate of combustion was found to be directly proportional to the oxygen concentration as is shown in Fig. 17. The relevant data together with the results is given below and in Tables 13 and 14.

(a) Combustion of Clyde coke 11 of ash content 14.2 per cent.
Specimen 1.91 cm. diameter and 3.18 cm. in length.
Diameter of combustion chamber 5.09cm.
Temperature of combustion chamber 1200° C.
Linear velocity of gas flow 190 cm. per sec.
Volume rate of gas flow 62.4 ml. per sec.
Pressure in combustion chamber 7.7 cm.

(b) Combustion of Electrode Arc Carbon of ash content 0.5 per cent.
Specimen 1.26 cm. diameter and 3.18 cm. in length.
Diameter of combustion chamber5.15 cm.
Temperature of combustion chamber 1240° C.
Linear velocity of gas flow 209 cm. per sec.
Volume rate of gas flow 71.4 ml. per sec.
Pressure in combustion chamber 8.0 cm.

Table 13. Experimental results of Series V11.

(a) Clyde Coke 11.				(b) Electrode Arc Carbon.			
O_2 %	R x 10^{-3}	O_2 %	R x 10^{-3}	O_2 %	R x 10^{-3}	O_2 %	Rx 10^{-3}
21.3	2.76	50.3	7.46	21.0	2.88	61.3	7.81
21.8	2.88	54.0	8.13	21.0	2.85	73.4	9.09
23.8	3.70	59.3	9.09	28.7	4.15	73.8	10.0
27.3	3.70	-	-	31.3	4.88	81.1	10.4
29.0	4.03	-	-	31.3	4.72	81.1	10.4
31.9	4.35	-	-	35.0	4.83	89.3	11.4
35.2	5.29	-	-	35.0	4.55	89.3	11.8
36.2	6.17	-	-	40.0	5.26	89.3	11.8
39.4	5.15	-	-	40.0	5.26	100.	12.4
40.1	5.43	-	-	55.0	7.35	100.	13.3
41.0	5.75	-	-	55.0	6.94	100.	11.5
47.6	6.90	-	-	61.3	8.70	73.8	9.52
50.1	7.25	-	-	61.3	8.55	-	-

Table 14. Calculated values for Series V11.

	(a)	(b)
$\bar{u}$ x 10^{5}	1.07	1.09
ρ x 10^{-5}	2.68	2.71
η x 10^{-4}	5.98	6.08
l x 10^{-4}	6.25	6.19
t x 10^{-2}	1.67	1.65
$\bar{x}$	0.86	0.86
(D - d)/2	1.59	1.94

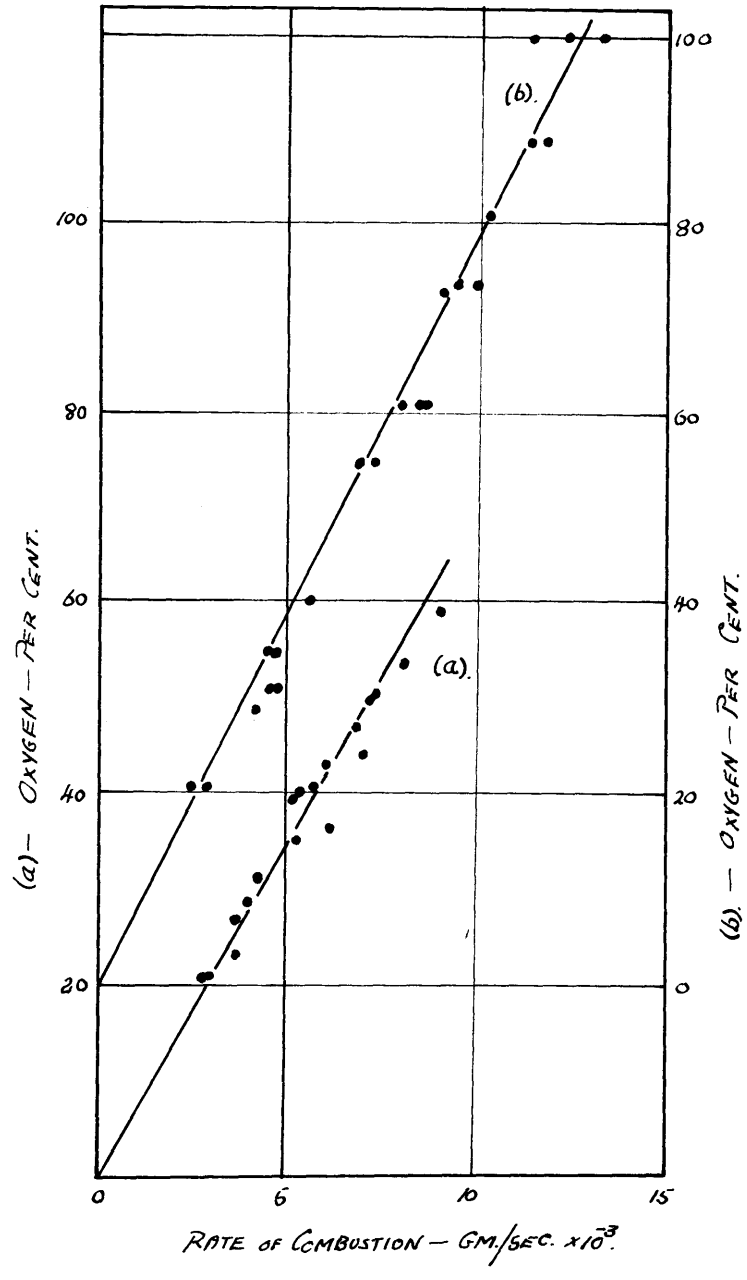

Fig. 17.- Variation of rate of combustion with the percentage of oxygen in the gas stream.

The two reaction equations calculated from Equation (11) are

$$(a)\quad R = K(14.3 \times 10^{-5} \times S) \quad gm. \text{ per sec.}$$

$$(b)\quad R = K(11.4 \times 10^{-5} \times S) \quad gm^{\frac{1}{2}} \text{ per sec.}$$

i.e., there is a linear relationship between the rate of combustion R and the percentage of oxygen in the gas stream S. The values of K found for the above equations are

$$(a)\quad K = 1.00$$

$$(b)\quad K = 1.12$$

Conclusions

The foregoing experiments do emphasize the complexity of the problems involved when considering the combustion of even a single carbon specimen in a cylindrical combustion chamber. Previous work has been verified in that it has been shown that the rate of combustion is proportional to the superficial surface area of the specimen. The variables of gas pressure , linear gas velocity, volume flow rate and diameter of the combustion chamber are mutually interdependent, an alteration in one affecting one or more of the others. By investigating the effect of one variable at a time an attempt has been made to combine their effects in a single comprehensive hypothesis in which it is suggested that since the mean displacement of a gas molecule is restricted by numerous collisions with its neighbours only a limited proportion of the oxygen supplied may be able to take part in the combustion reaction, the rest being swept out of the combustion chamber before it has a chance to diffuse across to the zone of combustion. This mean molecular displacement has been calculated from a simple formula derived from the elementary

kinetic theory of gases; although its actual numerical value may be in error the chief concern is with the way in which it changes in relation to the other factors such as pressure and linear gas velocity, etc.

This preliminary work was necessary before studying the effect of temperature on the rate of combustion and indeed it will be shown in the next Chapter that a variation in temperature causes a change in the mean molecular displacement $\bar{x}$ and hence in the volume of oxygen available for oxidation of carbon. It will be realised from this that before comparing the work of different investigators it is important to see whether or not their experiments have been conducted under comparable conditions particularly with regard to the proximity of the combustion chamber walls to the specimen, as molecular deflections from the wall can cause an increase in combustion rate as has been shown on p. 42. Similiar remarks apply to the comparison of the combustion rates of different cokes and it is desirable that conditions be chosen such that $\bar{x}$ is considerably smaller than $(D - d)/2$ as this range is much more amenable to mathematical treatment, deflections from the walls being unable to influence the number of oxygen molecules available for combustion as in Series V for example.

CHAPTER V

THE EFFECT OF TEMPERATURE ON RATE OF COMBUSTION

It was assumed in Chapter IV that all the oxygen molecules in the gas flow were equally capable of reacting with carbon (p.38 for example). In actual fact it is well known that before a molecule can take part in a chemical reaction it must possess a certain amount of energy, such molecules being termed ~~activated~~ activated molecules, i.e., only a fraction of the oxygen molecules supplied are able to take part in the combustion reaction in the foregoing experiments and this was the principle reason for introducing the constant K in Equation (11). Arrhenius suggested that there exists an equilibrium between these activated molecules and the normal ones, the former being formed from the latter by a collisional mechanism. Statistical considerations show that the number of molecules with an energy exceeding an amount E is proportional to a function containing the exponential factor

$$e^{-E/RT}$$

where E is the activation energy. Hence the rate of reaction is given by the expression

$$Ae^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

R being the gas constant, T the temperature in $^{\circ}$ A. and A a quantity which is substantially independent of temperature. For the present series of experiments it was decided for purposes of comparison to consider the rate of combustion per unit area of the standardized specimen, i.e.,

$$R_A = \frac{\text{Rate of combustion of standardized specimen in gm. per sec.}}{\text{Superficial surface area of standardized specimen in cm.}^2}$$

Hence, considering T as the only variable affecting the rate of combustion and utilising Equation (12)

$$R_A = Ae^{-E/RT} \quad \ldots\ldots(13)$$

$$\text{or} \quad \log_e R_A = \log_e A - E/RT$$

$$\text{i.e.,} \quad \log_e R_A = B - E/RT \quad \text{where B is a constant} \quad \ldots\ldots(14).$$

Hence a plot of $\log_e R_A$ against $1/T$ for specimens burnt at different temperatures should give a straight line graph of slope $-E/R$. The quantity E has the dimensions of energy and if R is taken as 1.98 calories then E will be obtained in calories per gm. mol. This type of treatment has been adopted by the majority of workers on activation energy and it is used here for purposes of comparison with their results.

It was decided to perform several sets of experiments in which the only variable was to be the temperature of the combustion chamber. As will be shown later on, the value of $\bar{x}$ introduced in the last Chapter will vary with the variation in temperature and in order to take this factor into consideration it was necessary to adjust the conditions of combustion in such a way that $(D - d)/2$ was always greater than $\bar{x}$. Four seperate sets of experiments were carried out and the data relating to the material used and other pertinent information is given below.

(a) Combustion of electrode arc carbon of ash content 0.5 per cent. Specimen 1.26 cm. diameter and 3.18 cm. in length.

Pressure in combustion chamber 8.0 cm.

Volume rate of air supply 75.5 ml. per sec. at N.T.P.

Total superficial surface area of specimen 15.2 $cm.^2$

$(D - d)/2 = 1.94$ cm.

(b) Combustion of Clyde coke No. 1V of ash content 13.0 per cent.

Specimen 1.91 cm. diameter and 3.18 cm. in length.

Pressure in combustion chamber 7.76 cm.

Volume rate of air supply 70.9 ml. per sec. at N.T.P.

Total superficial surface area of specimen 24.70 $cm.^2$

$(D - d)/2 = 1.62$ cm.

(c) Combustion of Consett Foundry coke of ashcontent 9.9 per cent.

Specimen 1.83 cm. diameter and 3.18 cm. in length.

Pressure in combustion chamber 8.0 cm.

Volume rate of air supply 69.4 ml. per sec. at N.T.P.

Total superficial surface area of specimen 24.4 $cm.^2$

$(D - d)/2 = 1.66$

(d) In this series of experiments conditions were exactly the same as in (c) except for the ash in the coke. Specimens of Consett Foundry coke similiar to those used in (c), were placed under a concentrated aqueous solution of sodium silicate and they were then evacuated for 1 hour. After removal from the solution the specimens were allowed to drain and finally dried at 120° C. in the usual manner.

The experimental combustion rated for the four sets of experiments are given in Tables 15 (a), (b), (c) and (d) the results being plotted in Figs. 18 and 19.

Table 15 (a). Variation of rate of combustion with temperature

T° C.	R gm./sec. $\times 10^{-3}$	$1/T^{\circ}$ A. $\times 10^{-3}$	$-\log_e R_A$
889	1.72	0.861	9.088
899	1.74	.853	9.075
976	1.87	.801	9.002
990	2.01	.792	8.930
1051	2.35	.755	8.775
1089	2.51	.734	8.708
1104	2.65	.726	8.654
1208	2.88	.675	8.572
1216	3.06	.672	8.515
1239	2.85	.661	8.573
1240	2.88	.661	8.585
1249	3.05	.657	8.517
1334	3.51	.623	8.375
1338	3.53	.621	8.366
1413	4.18	.593	8.275
1452	3.46	.580	8.385
1465	3.88	.575	8.278

Table 15 (b). Variation of rate of combustion with temperature.

T° C.	R gm./sec. $\times 10^{-3}$	$1/T^{\circ}$ A. $\times 10^{-3}$	$-\log_e R_A$
739	1.16	0.988	9.965
758	1.83	.971	9.510
848	1.92	.892	9.461
885	3.09	.864	8.987
893	2.83	.855	9.170
964	3.20	.809	8.948
975	3.01	.800	9.011
1059	3.19	.751	8.956
1060	3.58	.752	8.839
1129	3.97	.713	8.734
1148	3.41	.704	8.888
1180	3.50	.688	8.860
1190	3.70	.685	8.806
1235	4.12	.662	8.698
1295	3.57	.638	8.839
1298	4.08	.637	8.710
1303	4.15	.635	8.692
1304	3.82	.634	8.772
1330	4.10	.625	8.704
1486	4.81	.569	8.543
1496	4.59	.565	8.590

Table 15 (c). Variation of rate of combustion with temperature.

T^{o} C.	R gm./sec. x 10^{-3}	$1/T^{o}$ A. x 10^{-3}	$-\log_e R_A$
865	2.72	0.638	9.103
873	2.92	.873	9.032
969	3.16	.805	8.951
970	3.27	.804	8.915
1072	3.31	.750	8.902
1090	3.17	.734	8.947
1092	3.51	.733	8.847
1115	3.78	.720	8.771
1185	3.84	.686	8.757
1217	3.61	.671	8.819
1270	3.98	.648	8.723
1275	4.37	.646	8.628
1293	3.52	.639	8.841
1295	4.16	.638	8.675
1296	4.05	.638	8.704
1297	4.05	.637	8.705
1304	4.07	.634	8.696
1306	3.65	.633	8.808
1306	4.36	.633	8.630
1309	4.26	.632	8.653
1402	4.39	.597	8.623
1407	3.98	.595	8.720
1424	4.51	.589	8.594

Continued on next page-

Continuation of Table 15 (c)-

1428	4.44	.588	8.610
1460	4.46	.577	8.605
1463	4.53	.576	8.589

Table 15 (d). Variation of rate of combustion with temperature

T° C.	R gm./sec. x 10^{-3}	$1/T^{\circ}$ A. x 10^{-3}	$-\log_e R_A$
915	2.80	0.842	9.072
944	3.04	.823	8.990
1026	3.58	.770	8.826
1149	3.77	.703	8.775
1191	4.00	.683	8.716
1244	3.51	.659	8.846
1281	4.17	.644	8.675
1294	4.03	.638	8.707
1301	4.02	.635	8.710
1302	4.10	.635	8.690
1321	4.15	.627	8.679
1339	4.24	.620	8.657
1448	4.35	.581	8.631
1451	4.65	.580	8.565
1456	4.33	.578	8.636

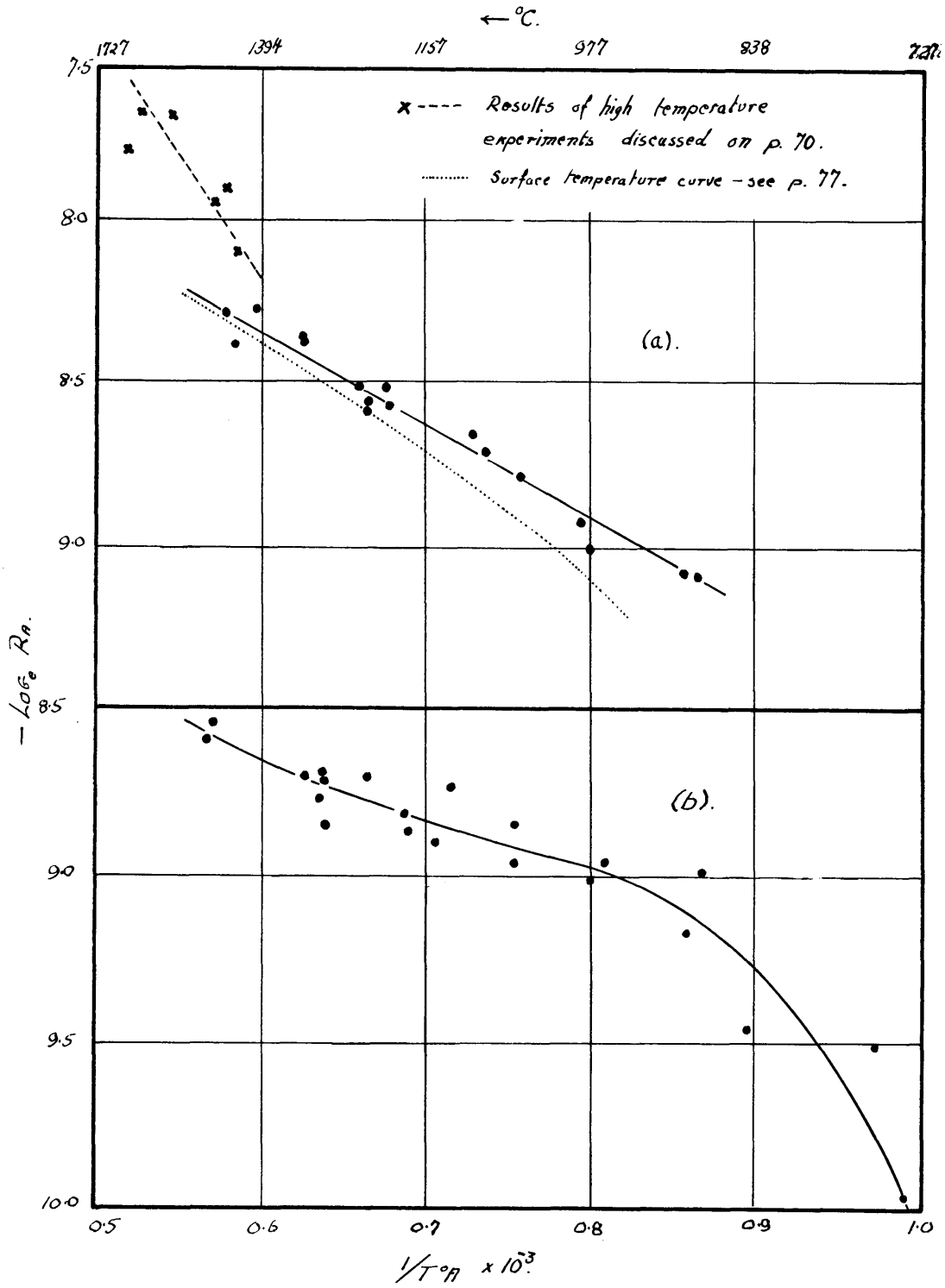

Fig. 18.-Variation of rate of combustion with temperature.

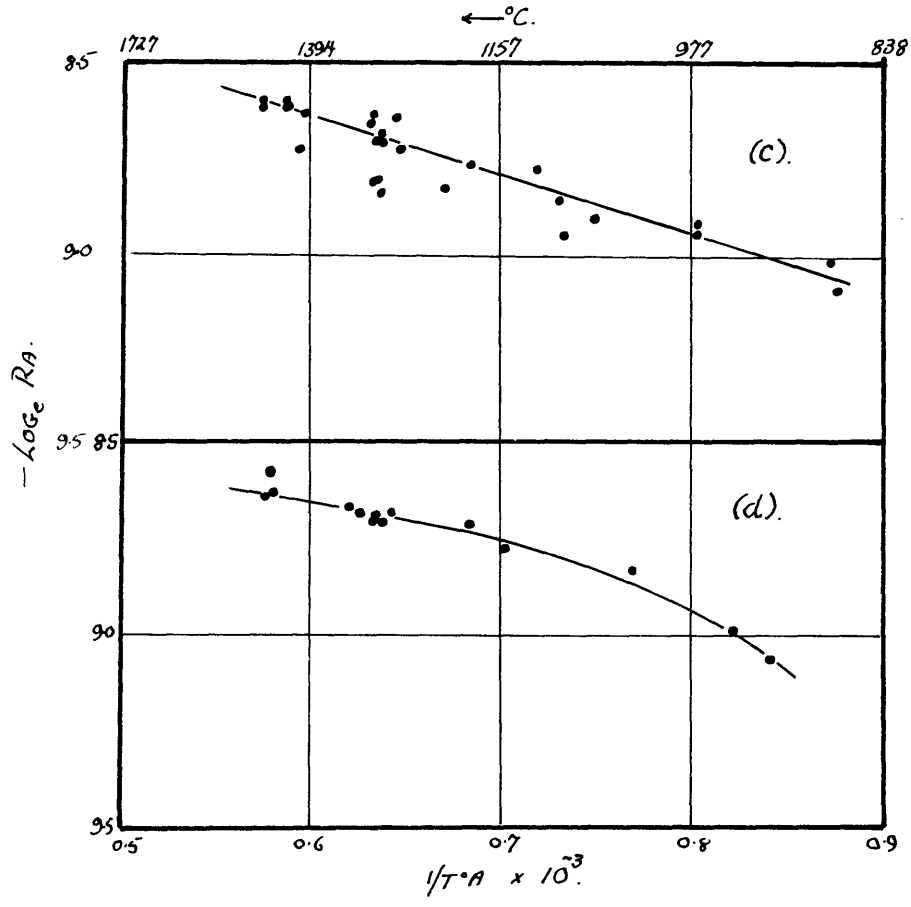

Fig. 19.- Variation of rate of combustion with temperature.

Curve (a) of Fig. 18 shows a straight line relationship between $\log_e R_A$ and 1/T where T is expressed in $^{o}\mathring{A}$. The value of E obtained from the graph is 5663 calories per gm. mol. as compared with the value of 3814 calories which was obtained by Finniston for a manufactured graphite. The results of the higher temperature experiments of p. *70* are also included in Fig. 18.

Curve (b) for a Clyde coke over the range of temperature 900° C. to 1500° C. gives an average value of for E of about 3300 calories per gm. mol. This curve may consist of two ranges, one above and one below the coking temperature of about 1050° C. although there is no evidence of a definite break in the curve as was obtained by Finniston[43]. The rate of combustion is seen to fall off rapidly below about 900° C., reaction rates in this lower temperature range being extremely susceptible to small temperature variations. Similiar results at low temperatures were found by Finniston for coke and by Tu, Davis, and Hottel for brush carbon[38].

Curve (c) for Consett Foundry coke shows a straight line relationship giving a value for E of 3070 calories per gm. mol.

The purpose of the Series (d) was to investigate the relative effects of a solid and fused ash for specimens burning under similiar conditions. The effect of adding a compound such as sodium silicate was such as to lead to the formation of a fluid ash over the whole range of temperature investigated. It was hoped that any specific catalytic effect of the sodium silicate could be ascertained by comparing the rates of combustion in Series (c) and (d) in the range of temperature above 1300° C. where the ash was molten in

both cases. However, the experimental error of the determinations appears to be greater than any effect of the ash, either physical or chemical, on the rate of combustion. It was found that with a large percentage of sodium silicate in the coke the rate of combustion was lowered appreciably owing to the formation of a fused slag layer over a relatively large proportion of the coke surface. The conclusion to be drawn from experiments of this nature is that the physical nature of the ash has little effect on the rate of combustion except at high ash contents (above about 20 per cent.) when a fluid ash definitely retards combustion by covering an appreciable proportion of the carbon surface.

So far no mention has been made of the effect of temperature on $\bar{x}$ and its subsequent effect on rate of combustion. The value of $\bar{x}$ was calculated for each set of experiments at the three temperatures 900° C., 1200° C., and 1500° C. The value of the expression

$$\bar{x}^2 + 2\bar{x}r$$

occurring in the reaction equation (11) was also evaluated as shown in Table 16. It will be seen that to a high degree of approximation

$$\bar{x}^2 + 2\bar{x}r = \text{Constant} \times T^n$$

where T is the temperature in °A. and n another constant. Taking logs.

$$\log (\bar{x}^2 + 2\bar{x}r) = \text{Constant} + n \log T.$$

Hence by plotting $\log (\bar{x}^2 + 2\bar{x}r)$ against log T the value of n may be obtained as the slope of the curve. The values of n were found to be as follows:

Series (a) n = 0.38

Series (b) n = 0.37

Series (c) n = 0.36

Table 16. Calculated values at various temperatures

	Series (a)			Series (b)			Series (c) & (d)		
Values	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Calculated	900	1200	1500	900	1200	1500	900	1200	1500
$\bar{u} \times 10^{4}$	.956	1.07	1.18	.956	1.07	1.18	.956	1.07	1.18
$\rho \times 10^{-5}$	3.50	2.79	2.32	3.40	2.71	2.25	3.50	2.79	2.32
$\eta \times 10^{-4}$	5.23	5.98	6.66	5.23	5.98	6.66	5.23	5.98	6.66
$l \times 10^{-4}$	4.69	6.01	7.33	4.76	6.10	7.40	4.69	6.01	7.33
V_L	15.1	19.0	22.8	16.6	20.8	25.1	15.5	19.5	23.5
$t \times 10^{-2}$	2.10	1.67	1.39	1.92	1.53	1.27	2.05	1.63	1.35
$\bar{x}$	.792	.847	.893	.763	.816	.858	.783	.836	.880
$\bar{x} + 2\bar{x}r$	1.64	1.79	1.93	2.04	2.23	2.38	2.05	2.23	2.38

It will simplify calculations and be sufficiently accurate for the treatment here to put

$$n = 0.5$$

when the reaction equation (11) may be written in the form

$$R_A = A' e^{-E/RT} \times T^{1/2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

where A' is a constant. Hence

$$\log_e R_A/T^{\frac{1}{2}} = B - E/RT$$

where B is a constant. Hence a plot of $\log_e R_A/T^{\frac{1}{2}}$ against 1/T should give a straight line graph of slope -E/R. When the results

of Series (a), (b) and (c) are plotted in this manner it is found that the curves are approximately linear and the values of E as calculated from the slopes of the curves are

Series (a).....E = 4210 cals. per gm. mol.

Series (b).....E = 1860 cals. per gm. mol.

Series (c).....E = 1630 cals. per gm. mol.

It has been assumed throughout the above discussion that the term $e^{-E/RT}$ is the only one which varies substantially with temperature. However, for a collisional reaction -

$$\text{Rate of reaction} = Ae^{-E/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$= \text{Constant} \times \bar{u} \times e^{-E/RT}$$

$$= kT^{\frac{1}{2}}e^{-E/RT} \quad (\text{since } \bar{u} \propto T^{\frac{1}{2}}) \ldots\ldots (16)$$

where $\bar{u}$ is the root mean square velocity of the molecules and k is a constant which is independent of temperature.[51]

Hence if the variation of $\bar{x}$ with temperature is taken into consideration as well as the above then, combining Equations (15) and (16) it is seen that

$$R_A = \text{Constant} \times e^{-E/RT} \times T \ldots\ldots\ldots\ldots (17)$$

$$\text{i.e.,} \quad \log_e R_A = B - E/RT + \log_e T$$

$$\text{or} \quad \log_e R_A/T = B - E/RT \qquad \text{where B is a constant.}$$

It will be seen from this that a straight line of slope -E/R is to be expected when $\log_e R_A/T$ is plotted against 1/T. Such plots

have been made for Series (a), (b) and (c) and by drawing a straight line through the points the values of E were found to be as follows:

Series (a).....E = 2760 cals. per gm. mol.

Series (b).....E = 410 cals. per gm. mol.

Series (c).....E 0 190 cals. per gm. mol.

The conclusion to be drawn from these calculations is that if the results are treated in the simplest possible, i.e., if the value of E is calculated from a straightforward plot of $\log_e R_A$ against 1/T (it is actually more convenient to plot Naperian Logatithms and make a suitable adjustment during the calculations), then the value of E obtained is of the same order as that obtained by Finniston. However, if a correction is made for the variation of $\bar{x}$ with temperature, thenthe value of E is reduced by about 1450 cals. per gm. mol. in each case. Moreover, if a correction is made for the variation of A with temperature in the expression

$$\text{Rate of reaction} = Ae^{-E/RT}$$

then a further decrease in the value of E of about 1450 cals. is obtained. With the reactions usually encountered in metallurgical processes a change in E of 1 to 3000 calories would be relatively unimportant as the value of E generally lies between 25 and 75 kcal. per gm. mol.[52], but with the reactions dealt with here such a serious change represents a very error in the value obtained for E.

Several workers[1, 2] studying the fundamental combustion reactions by passing oxygen over electrically heated graphite filaments, have noted a break in the mechanism of combustion at a temperature of 1500 to 1600° C., the high temperature reaction being of zero

order. Strickland-Constable however found the reaction at high temperatures to be of the first order and he states that glow discharge at high temperatures tends to give a zero order reaction (see also p. 5). In view of the fact that the temperature range above 1500° C. is of such importance when considering the combustion of coke in the blast furnace, it was thought desirable to obtain some results in this range. Unfortunately owing to the shortage of high quality mullite tubes it was impossible to continue this work but it is felt that more information is required in this important zone above 1500° C. The furnace combustion chamber was modified for this work as shown in fig. 20. The inner tube of 2.54 cm. internal diameter was made of fused alumina and the travel of the gases supplied for combustion between the inner and outer tubes insured that it was preheated to the temperature of the combustion chamber before meeting the specimen. At temperatures above about 1600° C. the outer mullite tube softened and collapsed onto the alumina baffle plated as soon as a vacuum was applied. For this reason it was necessary to maintain the furnace permanently at a high temperature as the outer tube inevitably cracked if the furnace was allowed to cool down from such high temperatures owing to the contraction of the mullite tube. The results obtained are given in Table 17 and they have been plotted in Fig. 18 with those of Series (a). Using the modified apparatus it will be seen that the value of E appears to be much greater for these high temperature experiments (the same type of electrode arc carbon was employed for these experiments as that used in Series (a)), but more experimental work is required in this temperature range and it would be unwise to place too much reliance upon these figures at this stage. Moreover, it

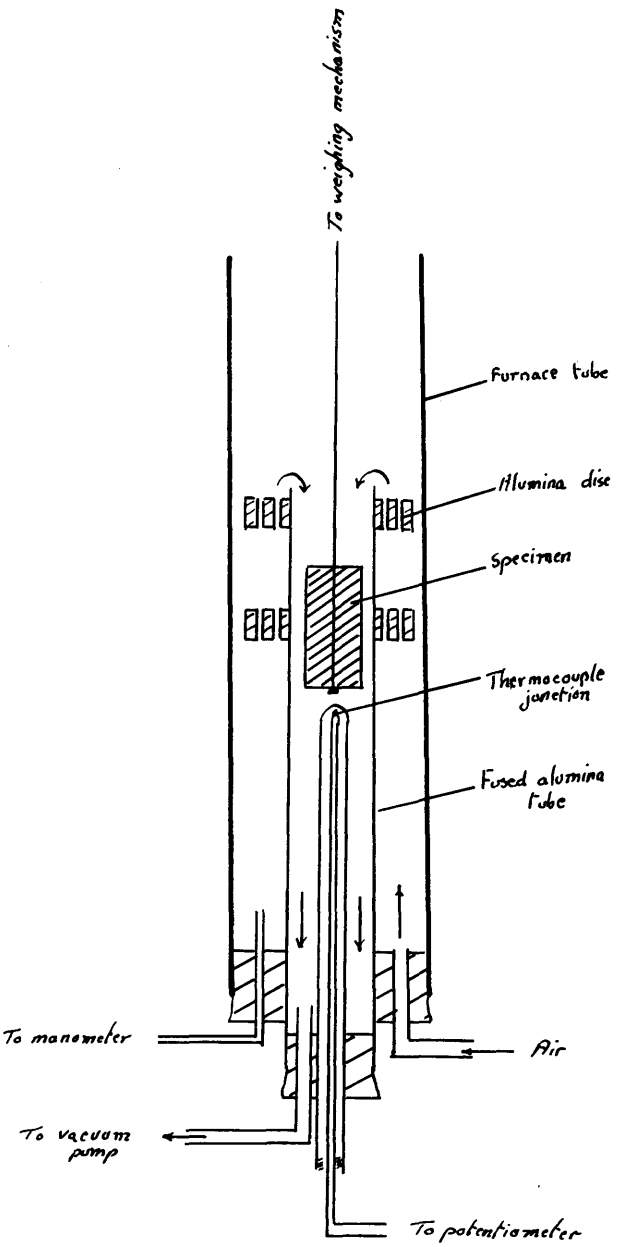

Fig. 20.- Modified apparatus for high temperature combustion experiments.

should be noted that the value of (D - d)/2 for this modified apparatus is 0.33 cm. whereas the value of $\bar{x}$ is still in the region of 1.0 cm., i.e., the walls of the combustion chamber will have a very pronounced effect on the rate of combustion (p. 57) and the variation of this effect with temperature may be responsible for the steeper slope of the graph in Fig. 18.

The details relevant to the high temperature experiments are as follows:

Combustion of electrode arc carbon of ash content 0.5 per cent.
Specimen 1.91 cm. in diameter and 3.18 cm. in length.
Pressure in combustion chamber 8.0 cm.
Volume rate of air supply 68.3 ml. per sec. at N.T.P.
Total superficial surface area of specimen.
(D - d)/2 = 0.33 cm.

Table 17. Results of high temperature experiments

T^{o} C.	R gm./sec. x 10^{-3}	$1/T^{o}$ A. x 10^{-3}	$-\log_e R_A$
1447	7.46	0.581	8.104
1467	8.93	.575	7.924
1486	8.62	.569	7.960
1564	11.7	.544	7.654
1626	11.9	.526	7.638
1665	10.5	.516	7.763

The Measurement of Actual Surface Temperature

It will have been realised that the temperatures quoted up to now have been the values obtained from a thermocouple placed

Plate 111.- Measuring the surface temperature of burning carbon.

1 cm. below the burning specimen. It is desirable however to know the actual surface temperature of the burning carbon. A platinum / platinum-rhodium thermocouple, protected by a thin silica sheath, was inserted into a $\frac{1}{8}$ in. (0.32 cm.) diameter hole drilled in the specimen as in Fig. 21. The specimen was then burnt in the normal way until the combustion zone reached the thermocouple, as depicted in Plate 111, when a maximum e.m.f. reading was obtained from the junction in the combustion zone. The temperature of the specimen as recorded by the above thermocouple is denoted by T_s and the maximum value or surface temperature by M. In actual fact the true surface temperature will always be greater than M (owing to thermal lag, conduction of heat along the thermocouple wires etc.) but this figure will be taken for the present. As it is impossible with this technique to weigh the specimen and record its temperature at the same time it becomes necessary to perform two separate experiments on two similiar specimens under similiar conditions, the first to determine R the rate of combustion and the second to determine M. In both cases a record is taken of the temperature as recorded by the thermocouple below the specimen, this being designated the furnace temperature T_f.

Experiments of this kind were found to be complicated by two systematic errors.

(1) Initially, before combustion commences, the two thermocouples should register the same temperature, i.e., $T_s = T_f$. However, it was found that there was nearly always a slight difference of up to $\pm 5^{\circ}$ C. This was apparently due to non-uniformity of the hot

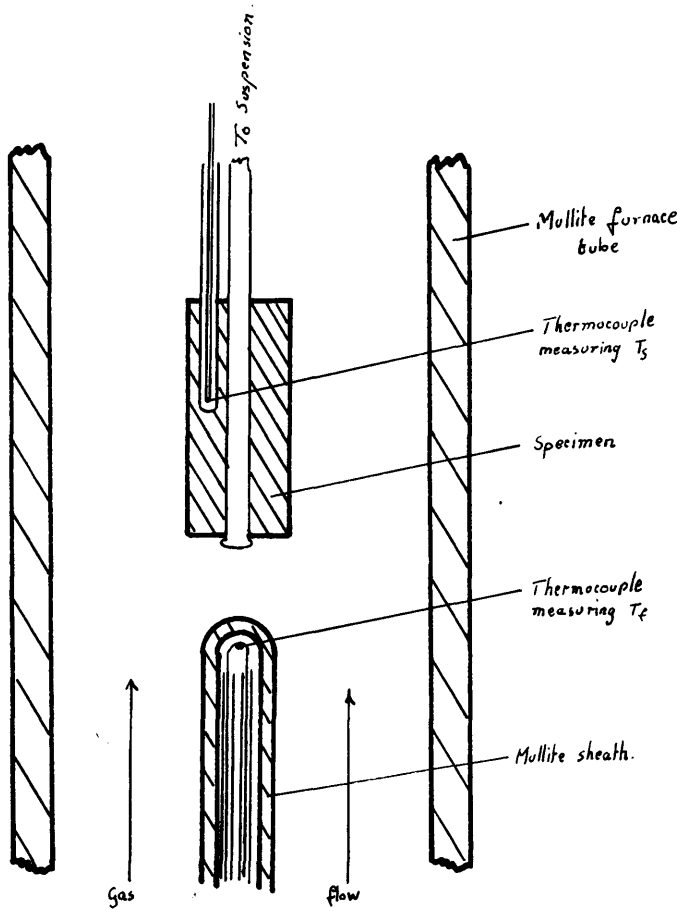

Fig. 21.- Method of measuring the surface temperature of burning specimens of carbon. Cross section through combustion chamber (actual size).

zone temperature, differences in the loss of heat along the thermocouple wires, differences in the emissivity of materials in the furnace hot zone, and small variations in thermocouple calibration. In connection with this latter point it should be mentioned that great care must be taken with a platinum / platinum-rhodium thermocouple encased in a thin silica sheath and working in the presence of carbon monoxide[53] and sulphur dioxide gases as in these experiments.

(2) The passage of gas through the furnace causes a redistribution of temperature quite apart from any heat liberated by combustion. Several "blank" experiments were performed using pure nitrogen gas (passed over red hot copper gauge and then through alkaline pyrogallol solution to remove possible traces of oxygen) and experiments were also carried out in which the carbon specimens were replaced by fired alumina cylinders of the same size. In all cases the temperature T_s rose to a value some 10 to 15° C. above that of T_f. The method eventually adopted for dealing with the results so as to give the greatest consistency of the experimental data was as follows.

If M is the maximum temperature as recorded by the thermocouple measuring specimen temperature T_s, and the initial difference of temperature recorded by the two thermocouples, i.e., the zero error is given by

$$\theta = T_s - T_f \quad ^\circ C.$$

Then the corrected surface temperature of the burning specimen is taken as

$$T_{ms} = (M - \theta) - 15 \quad ^\circ C.$$

the amount of 15 °C. being subtracted as an error due to the passage of gas through the furnace with subsequent disturbance of the hot zone. In this way a figure is obtained which would be correct if it were assumed that (1) T_f was correct and the zero error present in T_s alone and (2) the passage of and inert gas caused no temperature disturbance. The latter is a reasonable assumption for theoretical purposes as it implies that the gas, the specimen and the combustion chamber are everywhere at a uniform temperature and it enables one to compare the results for non-ideal cases.

A series of experiments was carried out under conditions similiar to those in the experiments discussed under Series Vll (a), (p. 54), but in this case each specimen was drilled with a hole for the insertion of the thermocouple measuring T_s, and the surface temperature was ascertained instead of the rate of combustion. The results are given in Table 18. For convenience, the temperature difference between the burning surface and the furnace temperature has been used in stating the results. In view of slight furnace temperature variations throughout the course of combustion it is better to note the maximum value of $(T_s - T_f)$, denoted by $(T_s - T_f)_M$, rather than the maximum value of T_s alone. The value of T_{ms} is then calculated from this value

$$\text{i.e.,} \quad T_{ms} = (T_s - T_f)_M - 15 + T_{f'} \quad °C.$$

where $T_{f'}$ is the value of T_f when $(T_s - T_f)$ is a maximum.

The appropriate values of R the rate of combustion have been taken from Fig. 17 (b) for the particular percentage of oxygen being employed. Fig. 22 shows the results as $(T_{ms} - T_{f'})$ plotted against the percentage of oxygen (a) and also as $(T_{ms} - T_{f'})$

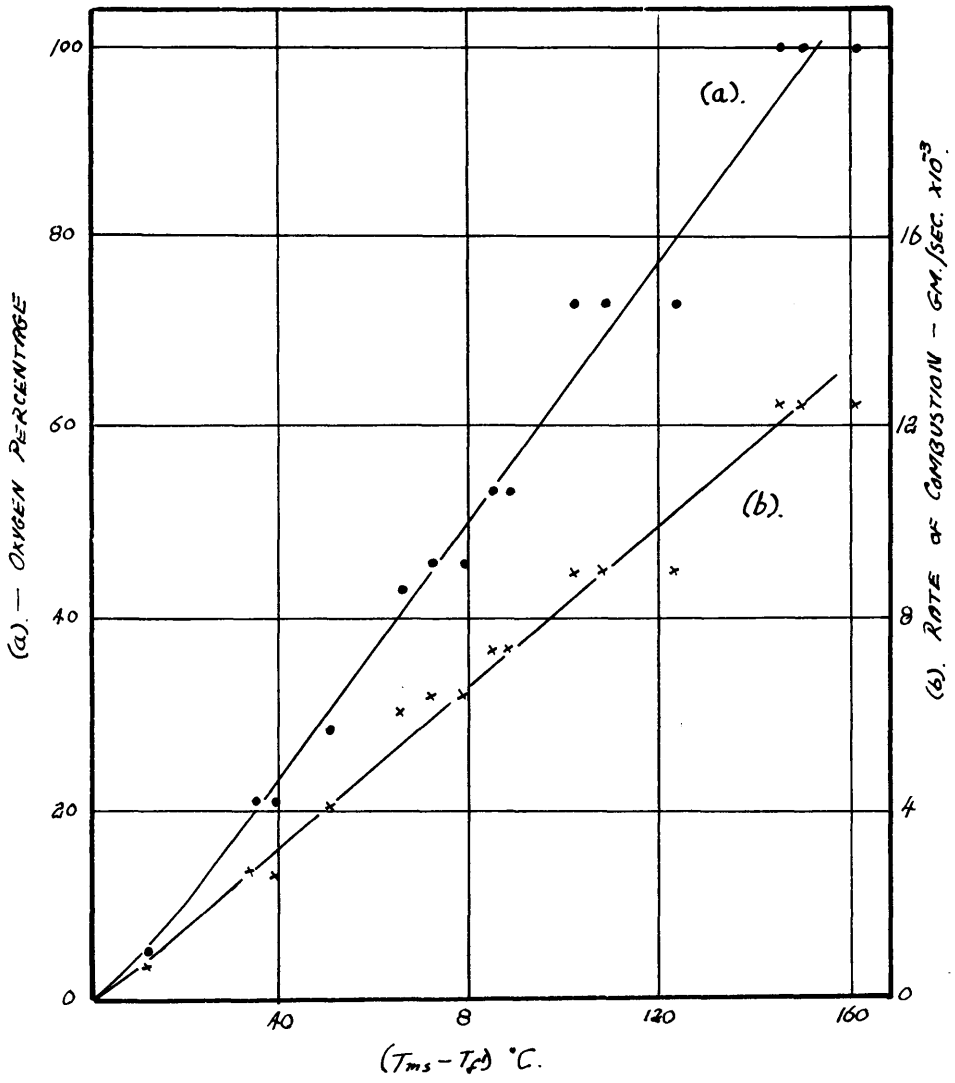

Fig. 22.-The effect of oxygen concentration and rate of combustion on the surface temperature of burning carbon.

against R (curve b). It is seen that the difference in temperature between the surface of the burning carbon and the furnace combustion chamber is directly proportional to the rate of combustion and also to the percentage of oxygen in the gas stream.

Table 18. Variation of surface temperature with oxygen concentration and rate of combustion.

Oxygen %	$T_{ms} - T_f$, °C.	R (gm./sec.) x 10^{-3}	Oxygen %	$T_{ms} - T_f$, °C.	R (gm./sec.) x 10^{-3}
0.0	0.	0.00	53.0	85	7.24
5.0	13	0.68	53.0	89	7.24
21.0	39	3.06	72.8	109	9.44
21.0	35	3.06	72.8	124	9.44
28.1	51	4.02	72.8	102	9.44
43.2	66	6.03	100.	150	12.4
45.9	72	6.36	100	161	12.4
45.9	79	6.36	100	145	12.4

Fig. 23 shows three typical sets of temperature-time curves for 21, 53, and 100 per cent. oxygen respectively. It will be observed that the temperature T_S reaches a value very close to the maximum immediately after combustion starts, thereafter there is a slow rate of increase in T_S until the maximum value of $T_S = M$ is reached when the burning surface actually reaches the plane of the thermocouple. As soon as the temperature of the specimen drops, which happens as soon as the supply of oxygen is stopped, the initial equilibrium conditions are rapidly established. Curves of a similiar form were found in every case and they illustrate the high thermal conductivity of the carbon material and the suprising fact that

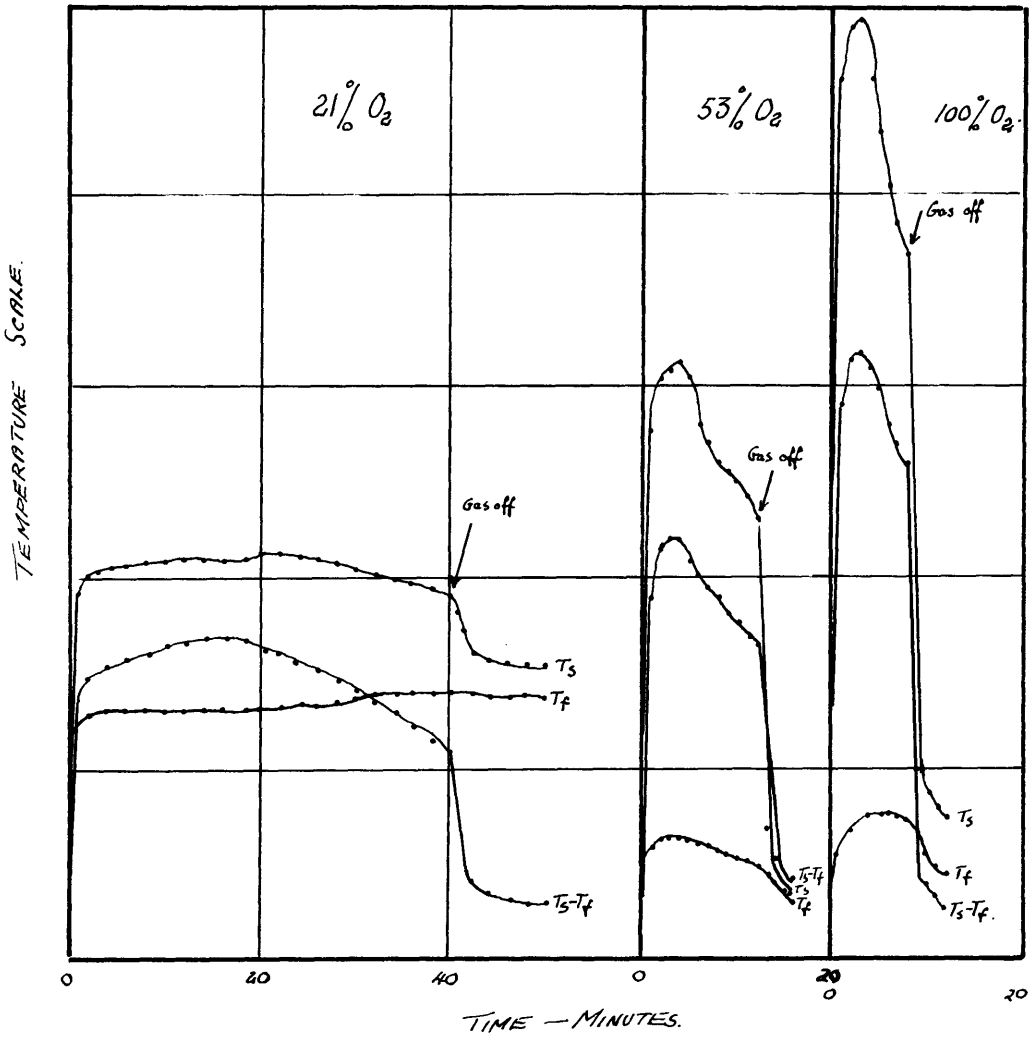

Fig. 23.-Typical sets of temperature-time curves for 21, 53 and 100 per cent. oxygen.

the whole specimen is at practically the same temperature as the burning surface layer.

Further experiments along similiar lines to the above were carried out in order to determine the effect of furnace temperature on the value of $(T_{ms} - T_{f'})$, i.e., the furnace combustion chamber temperature was made the variable and the oxygen concentration maintained constant at 21 per cent. The results are shown in Table 19, all other factors being kept at the same values as in the previous set of experiments. Fig. 24 is a graph of $(T_{ms} - T_{f'})$ plotted against furnace combustion chamber temperature T_f. The results show clearly that whereas at high temperatures (above say 1500° C.) it is reasonable to assume that the burning specimen is at the same temperature as the combustion chamber, the error of such an assumption becomes increasingly greater at lower temperatures.

Table 19. Variation of carbon surface temperature with temperature of combustion chamber.

$(T_{ms} - T_{f'})$ °C.	T_f °C	$(T_{ms} - T_{f'})$ °C.	T_f °C.
95	820	38	1204
84	896	39	1233
62	946	39	1234
60	974	35	1240
60	1024	27	1279
59	1033	32	1394
44	1104	9	1503
39	1164	-	-

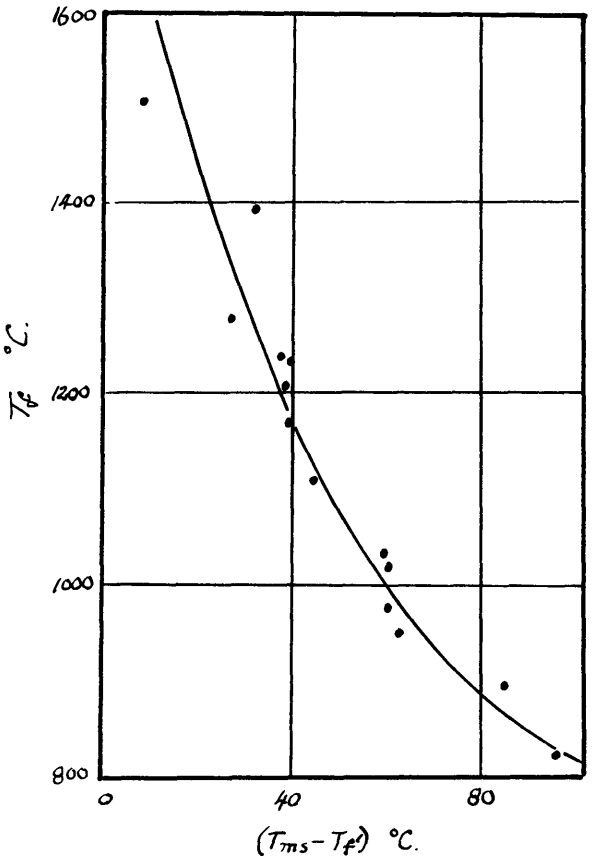

Fig. 24.-Variation of surface temperature with temperature of combustion chamber.

In the light of these experiments it is possible to revise the results shown in Fig. 18, curve (a), showing the variation of the rate of combustion of arc carbon with temperature. By the time gas molecules have reached the surface of the specimen they will have attained the temperature of the burning carbon surface and hence it is this value of T which should be used and not the temperature of the furnace combustion chamber. Since the determinations of Series (a) in Fig. 18 and also those of Fig. 24 were conducted under similiar conditions it is possible to obtain the surface temperature of the burning carbon for any given temperature of the combustion chamber and then plot a graph of rate of combustion against surface temperature. (The value $T = (T_{ms} + 15)$ °C. ½ is actually used as we are dealing with an experimental case and not idealized uniform conditions as mentioned on p. 74). Using the curves of Figs. 18 (a) and 25, the variation of $\log_e R_A$ with the reciprocal of surface temperature in °Å. is shown as the dotted line of Fig. 18 (a). Calculations similiar to those on p. 59 give an average value of E from this curve of 6600 cals. per gm. mol. as compared with the value of 5663 obtained when $\log_e R_A$ was plotted against the reciprocal of the combustion chamber temperature in °Å. These calculations emphasize the remarks made previously, i.e., when E is small as it is for the carbon plus oxygen reaction at these high temperatures, otherwise minor corrections become of enhanced importance. It seems desirable to use surface temperatures rather than combustion chamber temperatures for calculations of activation energy at normal pressures, but any errors introduced by not doing so will become increasingly less at higher temperatures and inthe case dealt with here may be neglected above about 1400° C.

Finally it was decided to see if any correlation existed between the rate of combustion of different cokes and the temperature of the surface when burning under similiar conditions. The experimental results are shown in Table 20 for four different cokes and an electrode arc carbon. All specimens were 1.91 cm. in diameter and 3.18 cm. in length, the rate of air flow and the pressure being the same as the previous experiments and the combustion chamber temperature was 1300° C. The average values of R and $(T_{ms} - T_{f'})$ have been plotted in Fig. 25. It will be seen that there is a tendency for more combustible cokes (as determined by these particular methods) to burn with a higher surface temperature. It should that as the combustion temperatures in these experiments are in the region of the ash fusion point for these cokes, this will almost certainly have some bearing on the value of the surface temperature.

Table 20. Surface temperatures for different cokes.

Type of coke	R x 10^{-3} gm./sec.	$(T_{ms} - T_{f'})$ °C.
Electrode Arc Carbon	3.52, 3.53 } 3.53	24, 23 } 23.5
Clyde Coke No. IV.	3.86, 3.80 } 3.83	34, 31 } 32.5
Consett Foundry Coke	3.98, 4.14 } 4.06	23, 26 } 24.5
Consett Wilputte Coke	3.42, 3.32 } 3.37	17, 19, 22 } 19.3
Dumbreck Foundry Coke	3.73, 3.68 } 3.71	18, 22 } 20.0

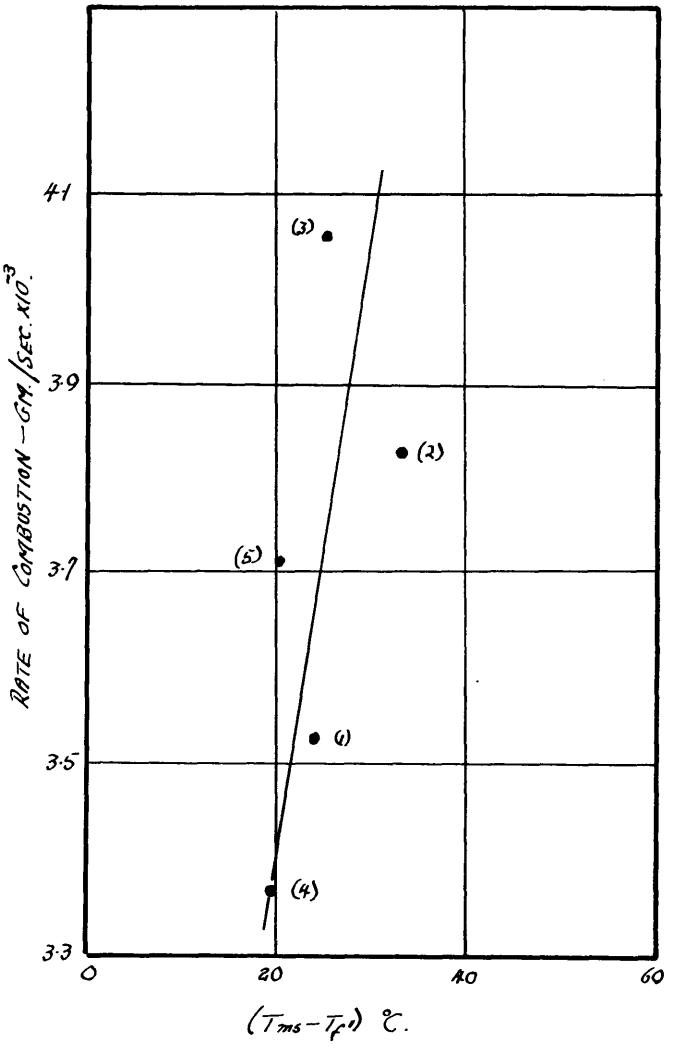

Fig. 25.-Surface temperatures of different specimens of coke and electrode arc carbon.

(1) Electrode Arc Carbon
(2) Clyde Coke No. 1V
(3) Consett Foundry Coke
(4) Consett Wilputte Coke
(5) Dumbreck Foundry Coke.

SUMMARY AND CONCLUSIONS

(1) An apparatus has been developed in which specimens of carbon can be burnt under controlled conditions of gas flow and at temperatures up to over 1650° C., the weight of the specimen, and hence the rate of combustion, being obtained by means of a simple mercury displacement balance which is easily operated under vacuum. So far as is known this method of weighing has not been used before and it has been found to be extremely adaptable and efficient.

(2) Previous work has been confirmed in that it has been shown that the rate of combustion of a carbon specimen is proportional to its superficial surface area.

(3) Experiments have been carried out under a wide variety of experimental conditions including changes in gas pressure, mass flow rate, linear gas velocity, oxygen concentration and dimensions of the combustion chamber. In an attempt to correlate the results obtained, use has been made of the conception of the mean displacement $\bar{x}$ of gas molecule in a time t in a similiar manner to that used in the study of the Brownian movement. In this way it has been shown that the governing factor controlling the rate of combustion of carbon in a moving gas stream is the number of oxygen molecules which can actually reach the carbon surface in the limited time available before these molecules are swept out of the combustion chamber. This work emphasizes the necessity of carrying out experiments under such conditions that the combustion chamber wall has little opportunity to interfere with the rate of combustion by the deflection of molecules from its surface. This preliminary work

was necessary before considering the effect of temperature on rate of combustion, as a change of temperature will cause a change in the mean molecular displacement $\bar{x}$ and hence in the number of oxygen molecules available for combustion.

(4) The variation of rate of combustion with temperature has been investigated over the range 750 to 1500° C. for both coke and electrode arc carbon. Previous work has again been confirmed in that it has been shown that the results are in accord with the Arrhenius conception of activation energy. The value of this activation energy was found found to be of the order of 3000 to 5000 calories per gramme molecule, a very low figure in comparison with most metallurgical reactions. In view of this low activation energy, several corrections which may normally be ignored in connection with work of this kind, become of great importance, and sufficient attention does not appear to have been drawn to this fact in previous literature. A few results were obtained at temperatures up to 1665° C. but more work is desirable in this temperature range before definite conclusions can be drawn. The above experiments have underlined the importance of comparing results under strictly comparable experimental conditions, particularly as regards furnace combustion chamber diameter and the proximity of the combustion chamber walls to the specimen.

(5) By inserting a thinly sheathed platinum/platinum-rhodium thermocouple into a hole drilled in the specimen an attempt has been to measure the true surface temperature of the burning carbon. The following conclusions are drawn:-

(a) The surface temperature is little different from the temperature of the interior of the specimen.

(b) The temperature of the specimen itself may be considerably higher than the temperature of the surrounding furnace combustion chamber (this temperature difference amounts to as much as 110° C. in these experiments) and other things being equal this temperature difference is directly proportional to the rate of combustion when various concentrations of oxygen are present in the gas stream.

(c) The difference between the temperature of the specimen and the temperature of the combustion chamber decreases rapidly with increase in combustion chamber temperature and is of the order of 15° C. at 1500° C.

(6) There appears to be little difference between coke and electrode arc carbon as regards rate of combustion and surface temperature during combustion, but the activation energy of arc carbon is slightly higher.

(7) It is suggested that more work should be carried out on the above lines at temperatures from 1500° C. upwards. This high temperature range is of the greatest importance from the point of view of combustion of coke in the blast furnace and moreover it is in this region that the greatest doubt exists as to the nature of the combustion mechanism and the magnitude of activation energies.

In conclusion, I would like to express my thanks to Professor R. Hay for his kind interest in this work, and also Dr. J. Taylor for his very helpful criticism and advice. I also wishto thank the British Coke Research Association who have been responsible for financing this research.

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